

**ULTRASONIC, VOLUMETRIC AND VISCOMETRIC STUDY
OF LIQUID MIXTURES CONTAINING
GLYCOLS AT DIFFERENT TEMPERATURES**

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BY

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ABSTRACT

The ultrasonic study is an area of piercing scientific and technological research. The study has earned penetrating significance in understanding the nature of molecular interactions and investigating the physicochemical behavior of ion-solvent interactions. This behavior of intermolecular interactions changes with the change in temperature, therefore, the thermodynamic study of liquid mixtures is of intense importance. For examining certain physical properties of the liquids in mixed solvent systems, the study of behavior of ultrasonic wave propagation is very effective. The thermodynamic study has been carried out to perceive the information regarding the interacting property of glycols in aqueous and mixed aqueous solutions. Effect of glycols on sugar alcohols have been studied by measuring ultrasonic, volumetric and viscometric properties at different temperatures using Anton Paar DSA 5000 M, Mittal enterprises ultrasonic interferometer, specific gravity bottle and Ostwald's viscometer. The ultrasonic speed, density and viscosity have been measured for the binary mixtures of ethylene glycol, diethylene glycol and triethylene glycol with glycerol at temperatures $T = (298.15, 303.15, 308.15 \text{ and } 313.15)$ K. With the help of these properties, various derived parameters such as acoustic impedance, adiabatic compressibility, intermolecular free length, relaxation time, ultrasonic attenuation, free volume, available volume, molar volume, Wada's constant, Rao's constant, Vander Waal's constant, internal pressure, enthalpy and Gibb's free energy are computed. The variation in these parameters have been discussed in terms of interactions prevailing in the binary systems. For the same binary systems, the deviation of experimental ultrasonic speeds from theoretical ultrasonic speeds is evaluated through several theoretical models namely the theoretical ultrasonic speed model given by Nomoto, Van Dael and Vangeel, Junjie and the impedance-based relation are incorporated. The deviation of experimentally obtained ultrasonic speed from the values obtained from different theoretical models is attributed to the fact that the theoretical models do not consider the effect of molecular interactions upon mixing of two or more components. Further, the densities and ultrasonic speeds of ethylene glycol, diethylene glycol and triethylene glycol in (0.00, 0.01, 0.03, 0.05) mol·kg⁻¹ aqueous solutions of glycerol have been measured at $T = (293.15, 298.15, 303.15, 308.15)$ K and experimental pressure $p = 0.1$ MPa. From the density data, the apparent molar volume V_ϕ , the partial molar volume V_ϕ^0 and the partial molar volumes of transfer ΔV_ϕ^0 have been calculated for glycols from water to aqueous glycerol solutions. Using ultrasonic speed values

apparent molar isentropic compression $K_{\phi,s}$, partial molar isentropic compression $K_{\phi,s}^o$ and partial molar isentropic compression of transfer $\Delta K_{\phi,s}^o$, have been evaluated. The pair and triplet coefficients have been computed from partial molar volumes of transfer and partial molar isentropic compression of transfer. The apparent molar isobaric expansion at infinite dilution $(\partial V_{\phi}^o/\partial T)_p$, second order derivative $(\partial^2 V_{\phi}^o/\partial T^2)_p$ have also been calculated. The parameters thus obtained have been discussed in terms of (solute-solute)/(solute-solvent) interactions prevailing in the ternary system along with structure making/structure breaking tendency of glycols in aqueous glycerol solutions. The intermolecular interactions of glycerol with two polyethylene glycols i.e. polyethylene glycol-400 and polyethylene glycol-4000 in aqueous medium have also been examined from the measurements of density and ultrasonic speed at temperatures $T = (293.15, 298.15, 303.15, 308.15)$ K and experimental pressure $p = 0.1$ MPa. The apparent molar volume (V_{ϕ}), partial molar volume (V_{ϕ}^o) and partial molar volume of transfer (ΔV_{ϕ}^o) have been evaluated from density data for polyethylene glycols from water to aqueous glycerol solutions. The limiting apparent molar expansibilities have also been evaluated. The ultrasonic speed measurements are used to determine apparent molar isentropic compression ($K_{\phi,s}$), partial molar isentropic compression ($K_{\phi,s}^o$) and partial molar isentropic compression of transfer ($\Delta K_{\phi,s}^o$) for polyethylene glycols from water to aqueous glycerol solutions. From (partial molar volume and partial molar isentropic compression) of transfer, the pair and triplet coefficients are calculated. By the perusal of these determined parameters, the results have been explicated based upon the competing patterns of physicochemical interactions of co-solutes and the solvents. In addition to it, the combination of volumetric and acoustical studies is used to investigate the interactions of ethylene glycol, diethylene glycol and triethylene glycol with Sorbitol as a temperature's function. Densities and ultrasonic speeds of ethylene, diethylene and triethylene glycol in (0.00, 0.01, 0.03, 0.05) mol·kg⁻¹ aqueous solutions of sorbitol are measured at temperatures $T = (288.15, 298.15, 308.15, 318.15)$ K and experimental pressure $p = 0.1$ MPa. With the help of density data, (apparent molar and partial molar) volume, V_{ϕ} and V_{ϕ}^o are computed. The values for partial molar expansibility $(\partial V_{\phi}^o/\partial T)_p$ and second order derivative $(\partial^2 V_{\phi}^o/\partial T^2)_p$ have also been determined. From ultrasonic velocity values, (apparent molar and partial molar) isentropic compression, $K_{\phi,s}$ and $K_{\phi,s}^o$ are evaluated. Further the partial molar volumes of transfer ΔV_{ϕ}^o and partial molar isentropic compression of transfer $\Delta K_{\phi,s}^o$, are also calculated. The computed values of partial molar volumes

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DECLARATION

I hereby declare that thesis entitled, “**ULTRASONIC, VOLUMETRIC AND VISCOMETRIC STUDY OF LIQUID MIXTURES CONTAINING GLYCOLS AT DIFFERENT TEMPERATURES**” has been submitted by me for the degree of Doctor of Philosophy in Physics to the Lovely Professional University Phagwara is the result of my original and independent work under the guidance of Dr. Kailash Chandra Juglan. This work has not previously formed the basis for the award of any degree, fellowship, in this or any other University or Institute.

Date :

Kirandeep Kaur

Reg. No. 11412812

CERTIFICATE

This is to certify that Kirandeep Kaur has completed Ph.D. thesis entitled **“ULTRASONIC, VOLUMETRIC AND VISCOMETRIC STUDY OF LIQUID MIXTURES CONTAINING GLYCOLS AT DIFFERENT TEMPERATURES”** under my Guidance and supervision. To the best of my knowledge, the present work is the result of her original investigation and study. No part of the thesis has ever been submitted for any other Degree at any University or Institute.

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Signature of Co-Supervisor

Dr. Harsh Kumar

Associate Professor

National Institute of Technology

Jalandhar, Punjab

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LIST OF ABBREVIATIONS

c	Ultrasonic speed
ρ	Density of material
η	Viscosity
K	Kelvin (Temperature in absolute)
Z	Acoustic impedance
L_f	Intermolecular free length
M_{eff}	Effective molecular weight
τ	Relaxation time for binary mixture
V_f	Free volume
R	Rao's constant
W	Wada's constant
x_1	Mole fraction of solute
x_2	Mole fraction of solvent
Z	Acoustic impedance
β	Adiabatic compressibility
L_f	Intermolecular free length
α	Ultrasonic Attenuation
τ	Relaxation time
M_{eff}	Effective Molecular Weight
V_f	Free Volume
W	Wada's Constant
R	Rao's Constant
b	Vander Waal's Constant
V_m	Molar Volume
π_i	Internal Pressure
V_a	Available Volume
ΔG	Gibb's Free Energy
H	Enthalpy
V^E	Excess molar volume

ΔG^{*E}	Excess Gibb's free energy
ΔH	Excess enthalpy
$\Delta \eta$	Viscosity deviations
V_ϕ	Apparent molar volume
m_A	Molality of the solute
m_B	Molal concentration of cosolute
p	Pressure
Pa	Pascal
T	Temperature
V_ϕ^0	Partial molar volume
ΔV_ϕ^0	Partial molar volume of transfer
a, b, c	Constants of least square fitting of equation 4.4
E_ϕ^0	Partial molar expansibility
$K_{\phi,s}$	Apparent molar isentropic compression
k_s	Isentropic compressibility
$K_{\phi,s}^0$	Partial molar isentropic compression
$\Delta K_{\phi,s}^0$	Partial molar isentropic compression of transfer
S_V^*, S_K^*	Experimental Slopes
V_{AB}	Pair interaction coefficient for volume
V_{ABB}	Pair interaction coefficient for isentropic compression
K_{AB}	Triplet interaction coefficient for volume
K_{ABB}	Triplet interaction coefficient for isentropic compression
EG	Ethylene Glycol
DEG	Diethylene Glycol
TEG	Triethylene Glycol
PEG-400	Polyethylene Glycol-400
PEG-4000	Polyethylene Glycol-4000

1.1 ULTRASONICS

Ultrasonic is a branch of acoustics which deals with the generation, propagation and use of inaudible acoustic waves. It generally deals with the sound waves with the frequency higher than 20,000 Hz which is upper audible limit for human hearing. It also deals with the generation, propagation as well as the use of inaudible acoustic waves. These are the mechanical waves which require a physical medium to propagate through it [1]. Ultrasonic speed is one of the manners to obtain data about physical behavior of liquid mixtures and there exists number of models for determining it theoretically from observed factors. The Ultrasonic Testing employs high frequency sound energy to guide experiments and conduct measurements. Ultrasonic examination can be used for, dimensional –measurements, flaw detection, material characterizations and more. Ultrasonic inspection is a very versatile and useful NDT (Non-Destructive Technique). The ultrasonic testing is responsive to both subsurface and surface irregularity. It is highly accurate for determining and estimating shape and size of molecules. The NDT is used to test as it cannot cause disorder to the structure. This approach has a wide range of scientific and business analyses to investigate properties without causing any damage. The NDT has a number of non-destructive tests such as ultrasonic, magnetic particle, radiography and eddy current testing and low coherence of interferometry.

1.2 FREQUENCY RANGES OF SOUND

The Ultrasonic or Supersonics are the sound waves with frequency above 20 KHz whereas Infrasonic are the waves below 20Hz frequency. The mediums like Air, water and solids are the compressible in nature through which sound waves travel. For humans, audible sound frequency is 20 Hz to 20 KHz.

The bats use ultrasonic frequency for locating their prey and flying all around. The bats use variety of ultrasonic techniques to detect their prey. They have ability to produce and detect ultrasonic frequencies ranging from 100 KHz to 200 KHz. Many nocturnal insects like moths, beetles etc. produce ultrasonic frequencies to confuse bats and protect themselves. Dog is also a one of the animal which can hear ultrasound and moreover dog whistle is specially designed for dogs which produces ultrasound of 18-22 KHz. In case of marine life toothed whales and dolphins use

ultrasound for navigation and hunting the prey in deep ocean waters. The ultrasonic speakers are sold as electronic devices which are claimed to make away insects, also there is no scientific proof that this device working.

1.3 ULTRASONIC TECHNIQUES

In Ultrasonic techniques, ultrasonic waves are employed. Ultrasonic waves are the sound waves having frequency more than 20 KHz. Ultrasonic testing (UT) is a family of testing techniques which are non-destructive in nature which are further based on the propagation of ultrasonic waves. Ultrasonic waves are inaudible to human ear which can hear in between 20 Hz to 20 KHz. This range is known as sonic range. The frequencies lower than this range are known as Infrasonic and the frequencies above this range, called Ultrasonic. There are different methods to generate ultrasonic waves such as Mechanical Methods, Piezoelectric Generator and Magnetostriction Generator. The Mechanical method (Galton whistle) is of least application in research field as it produces frequency of 100 KHz so it is less used. The other two methods are preferred more as compared to this method. Piezoelectric Generator was developed by Langevin in 1917. This Piezoelectric Generator is most widely used in Ultrasonic Interferometers.

1.3.1 Magnetostriction Method: When a ferromagnetic rod is placed in magnetic field parallel to the length and rod then small change in length experiences. This technique is for producing low frequency ultrasonic waves. Magnetic field is applied parallel to the rod of ferromagnetic material. Due to magnetic field small contraction of material occur and change of length produces vibrations. Strength of magnetic field, temperature and nature of material effects the contraction. It is very simple and cheap but there will be hysteresis and eddy current losses.

1.3.2 Piezo-Electric Method: In this method electric field is applied to one face of crystal and there is change in dimension of crystal at the other faces. These contraction and relaxation of the faces the of crystal produces ultrasonic waves. The advantage of this method is that it is not affected by climate conditions as humidity

or temperature but the shaping of crystal needs precision. The converse of this effect is also true.

1.4 ULTRASONIC INVESTIGATIONS

The ultrasonic investigation of liquid mixtures and pure liquids consisting non-polar and polar components are significantly important in analyzing intermolecular interactions between component molecules. These investigations are helpful in giving out acute observations into structure and various bonding of associated molecular complexes and other related molecular processes. It helps in depicting the molecular association and dissociation. These are of considerable importance for determining the thermo-acoustical or physico-chemical behavior of liquid mixtures and the respective measurements are used to evaluate the molecular interaction among the liquids [2]. It plays a significant role in understanding the strength and nature of molecular interactions in binary or ternary mixtures. Different kind of liquid mixtures show various usual or unusual characteristics which gains substantial attention [3, 4]. In medical science, the waves are being used for medical diagnosis, for detection of cancer tumors, bone fractures and physiotherapy, gynecology, bloodless surgery, cardiology, etcetera [5]. The thermodynamic and ultrasonic studies of molecular interactions are of huge importance in developing theoretical models as well as its application in industry and engineering [6]. There are many types of interactions occur between the solutes and solvents in the solutions and the study of these interactions is of great interest in various branches of physics and chemistry, these interactions provide the better understanding of nature of solute and solvent, i.e. does the solute distorts or modifies the solvent? The structural arrangement is influenced by the mutual interactions as well as the shape of the molecules [7, 8]. The departure from linearity in the acoustical parameter versus concentration in the liquid mixture is considered as the proof of existence of molecular interactions between various species [9-11].

When two or more liquids are mixed together, then they result in change of their physical and thermo dynamical properties which can be considered as a sum of several contributions due to change in free volume, steric hindrance, energy and

molecular orientation [12]. Weak molecular interactions can also be detected by ultrasonic technique. The chemical and physical properties of liquid mixtures have been studied by various workers and they co-related the linear or non-linear variation of ultrasonic speed, compressibility, free volume and other related thermo-acoustic parameters with structural changes happening in the liquid with the variation in concentration of liquid mixture [13]. The liquid mixture studies are indispensable for many chemical processes, including phase equilibrium, solubility effects, calculation of speciation, absorption and distribution of drug and drug products [14]. The compressibility nature of solutes is a very sensitive indicator of molecular interactions and provides useful information [15]. Further, the polymer dissolution is of great importance in understanding the concept for dissolution process allows the optimization of design and in many industrial applications [16]. The linear increasing trend of interaction parameter is associative which strongly supports the interaction between solute-solvent molecules [17, 18]. The ultrasonic studies can provide interesting information on the specificities of ion-solvent interaction related to the structure of the solute and the reciprocal effects which arise in the solvents [19, 20]. When binary or more complex mixtures are to be used as a solvent, specific solvent and co-solvent interactions can intrude to modify the structural properties and molecular arrangement of the pure liquids [21]. Ultrasonic measurement in cooperation with density and viscosity data provide huge information about the interaction between ions, hydrogen bonding, dipoles, dispersive and multi-polar forces [22]. It has been observed from the previous studies that the mixed solvents have more practical importance rather than pure liquids in most of the chemical and industrial processes as they provide varied range of composition so as to permit continuous adjustment of desired properties of the medium.

The ultrasonic along with volumetric and viscometric studies have gained huge consequence in investigating the physico-chemical aspects and finding the nature of molecular interactions of binary or ternary liquid systems [23]. The ability of ultrasonic technique to characterize the physico-chemical behavior of the liquid mixture, have made it a powerful tool for studying the molecular interactions [24]. Although the molecular interactions can be best carried out through spectroscopic or

non-spectroscopic methods such as dielectric or magnetic but the ultrasonic technique is considered to be the best of all to determine the type of interactions or any kind of structural change in the liquid system [25, 26].

The properties of liquid mixtures can be altered continuously within a reasonable range by varying composition of the mixture till an optimum value of some desired parameter is attained [27, 28]. Generally, acoustic parameters depend on the ratio of molar volume of the liquid to the real volume of the molecules in a mole of the liquid (molecules are treated as rigid balls with the uniform radius r) [29]. Self-association between alcohol molecules decreases with increasing concentration of the non-polar solvent while the displacement of solvate equilibrium is determined by physical properties of hydrocarbon solvent [30-32]. Ultrasonic speed, like any other physico-chemical property in binary liquid mixtures could be related either to size and shape of the molecules or entropy effect connected because of volume and space filling effects with mixing processes [33, 34]. The intermolecular forces responsible for the molecular interactions can be classified as long-range forces and short-range forces. The long-range forces are the electrostatic induction and dispersion forces and they arise when the molecules come close enough causing a significant overlap of electron clouds and are often highly directional [35-38].

Studies on acoustic parameters have become so prominent in the recent years. To understand solution, it is necessary to understand the solvation behavior of binary mixture system. Acoustic parameters are responsive to changes and are important in illuminating the solvent-solvent interaction. The ultrasonic speed measurements have been successfully used to examine and determine strong and weak molecular interactions present in the ternary and binary mixtures. Ultrasonic techniques are huge source of information about the structural and molecular changes in liquid mixtures. Within the framework of the theory of physical acoustics, such kind of techniques could also provide useful information about the mixing solution and its temperature dependence. The ultrasonic technique is an interesting and effective technique to analyze the physicochemical properties of liquid - liquid mixtures, electrolytic mixtures and polymeric solutions. These solutions find wide applications

in the medical, pharmaceutical, leather, textile, chemical and solvent solutions industries and the study, understanding and analyzation of the thermodynamic properties of mixtures and different solutions were most significant for their applications in these industries. The spread of ultrasound waves into a substance has become a major test to study its properties. Such studies, such as changes in temperature and concentration, are useful to obtain the insight into the structure and the various linkages of the bound molecular complexes and other related molecular processes. The velocity and the associated acoustic parameters help us to characterize the thermodynamic, physical and chemical aspects of liquid mixtures like association and dissociation of the molecules.

With a small size and quadrupole moment, liquid water is an exclusive solvent having capability to support wide hydrogen-bonding networks [39, 40]. Numerous studies are done on characteristics of molecular interactions of polar organic liquids and water [41-47]. As compared to pure liquids, mixed solvents have more practical significance in various chemical, pharmaceutical and industrialized processes as they offer large variety of mixture compositions of two or more components in different proportions such that incessant modification of the estimated properties can be permitted [48].

The use of chemicals in the medical field requires the attention of public in every area including the ultrasonic behaviour of liquids. Usually, ultrasonic research can be widely used to learn molecular interactions when combined with other water resources. Much of the study has been done in molecular interactions on products and mixtures in various forms of the body. In recent years, ultrasonic technology has been an effective way to find out about more efficient method for gaining information about behavior of solids and liquids having its capability of featuring the physiochemical behavior of medium.

1.5 ULTRASONIC TESTING

The Ultrasonic testing is based on capture and quantification of either the reflected waves (pulse-echo) or the transmitted waves (through-transmission). Each of the two

uses in various applications but pulse-echo systems are more useful since they require one sided access to the object inspected and tell a lot about concrete than a simple transmission. Back walls, significant voids can be detected by pulse-echo. Ultrasonic is a non-destructive technique to characterize the internal structure of test material through high frequency ultrasonic waves with commonly used frequencies range from 500 KHz to 20 MHz. The High frequency sound waves are very directional until they face a boundary with another medium, at which point they reflect back to source. There is a formation of standing waves and much can be inferred from the reflected wave for example, ultrasonic thickness measurement of metallic pipes and aircraft body. This method is employed to detect flaws in large metal pieces or materials. This method is used in many fields including industries, research, metallurgy, aerospace, automotive, medical and various other sectors.

1.5.1 DETECTION AND RANGING

NON-CONTACT SENSOR:

There is no need of contact with the target for an ultrasonic sensing system. That is why this process is very suitable for medical, military, pharmaceuticals and industries as these sensors don't contaminate liquids or clog the product. Here both the continuous wave and pulse systems are used. The main principle behind these sensors is that ultrasound is transmitted in a pulsed fashion and once transmitted, it waits for the return of the signal and received signals are processed again.

MOTION SENSORS AND FLOW MEASUREMENT: The common application of ultrasound is seen in automatic door openers where the ultrasonic detects the person and automatically opens the door. These sensors are also used to detect intruders. Moreover, these sensors are used in pipes to monitor the flow of gas or liquid within the pipes. In fluid mechanics the flow of fluid is measured with the help of ultrasonic flow meter.

ULTRASONIC RANGE FINDER: The main application of ultrasound is in Sonar., underground application. An Ultrasonic pulse is transmitted from the transmitter and

if there is an object between the path of ultrasound it will be reflected back to transmitter as an echo. By measuring the time difference between transmitting and receiving of signal can be employed to calculate the distance. Measured travel time also depends on the factors like temperature and salinity of water. Ranging in water varies from 100 to 1000 meters.

ULTRASOUND IDENTIFICATION: Ultrasonic Identification or also known as USID is a real time locating system. It is used to automatically track and identify location of the objects. Badges or tags are attached to objects which transmit ultrasonic signals to communicate their current locations. These are extensively used in military.

1.6 DSA (DENSITY AND SOUND VELOCITY ANALYZER)

The ultrasonic testing instrument that is prominently being used in the world is Anton Paar DSA 5000M (Density and Speed Analyzer) meter and is widely regarded as the most precise instrument for calculating the density and sound velocity. It determines the sound velocity and density in one cycle of the sample inspection. Its unique measuring system reduces the error margin for determining concentration for the binary mixtures. Quality analysis in production process, preparing solution and concentration measurements of ternary solutions are the other applications of this instrument.

Features of DSA:

- It automatically measures density and velocity of sound of binary and ternary samples.
- Automatic and simultaneous filling and cleaning of measuring cells.
- Fast and accurate measurement with the small sample volume.
- Permanent display of density and velocity of sound as well as calculated properties.
- Automatic viscosity correction across the sample's entire viscosity range.
- Detects the filling errors and gas bubbles within the sample and generates a sample warning.

- Displays and stores the live images of the oscillating U-tube sensor and the entire filled-in sample.
- Later review of these stored images guarantees completely transparent measurement processes.
- Removes the measurement drifts caused by temperature stress due to change in temperature or sample temperatures significantly different from measuring temperature.
- Neither the sample preparation nor the addition of reagents is required.

1.7 GLYCOLS

Like all other low-molar mass alcohols, glycols are solvable in whole amounts of water. By coupling action of glycols, various insoluble-water materials can be made clear solutions. Tremendous solubility is observed for aromatic compounds in glycols. Aromatic hydroxy compounds and alcohols like phenols are mixable in entire proportions.

Glycols absorb moisture from the air. If positioned in atmosphere comprising vapors of water, then moisture will be picked up and hold by the molecules. Because of this characteristic of glycols, these are cast off for various applications such as humectants and dehydrating agents. Most of such applications utilize glycol-water solutions. The characteristic of a glycol alters with addition of water into it. With the change in temperature and humidity, its humectant value got affected.

With temperature, glycols' viscosities change inversely. Glycol molecules at high temperature move freely and as the molecules of glycol cool, their viscosity keeps on increasing until their final settlement and failure of movement of molecules. These are much fluid than most of the plasticizers and solvents having high boiling points. Because of this purpose, to decrease the viscosities of liquid compositions, glycols are frequently casted off either alone or in association with other fluids.

Among the glycols, Ethylene Glycol (EG), Diethylene Glycol (DEG), Triethylene Glycol (TEG), Polyethylene Glycol-400 (PEG-400) and Polyethylene Glycol-4000 (PEG-4000) are few members of generally used homologous series of diols. The

hygroscopicity of these liquids is superlative for utilizing in printing inks, cellophane, fiber treatment, adhesive, paper, and leather.

Ethylene Glycols (EGs) are the liquids which are miscible in water in the whole composition range and due to their hygroscopic nature, are highly soluble in polar solvent owing H-bonding [49-51]. These glycols are broadly used in plastic industry where they are used in the preparation of polyethylene terephthalate which is used further to make plastic bottles for pharmaceutical and food industry [52-56]. Ethylene glycols (EGs) are the solvents possessing hydroxyl and oxy groups in same molecule because of which development of inter- and intramolecular hydrogen bonds between -O- and -OH groups has been observed [57].

1.7.1 ETHYLENE GLYCOL

Ethylene glycol is utilized in the coolant and anti-freeze industry. It acts as a coolant for the car engines. Ethylene glycol also finds its application in the fiber industry such as for manufacturing of the fiber glass which is used for the manufacturing of the bowling balls and bathtubs, also in the manufacturing of the polyester fiber clothing and the manufacturing of the packaging bottles and films. Most of the ethylene glycol products are recyclable, cost efficient and energy saving.

1.7.2 DIETHYLENE GLYCOL

Diethylene glycol finds its applications in different types of industry such as fuel industry, agriculture industry, paints and emulsion industry, fabric industry, automotive industry and de-icing and anti-freeze industry. It is utilized as a chemical intermediate for unsaturated polyester resin, polyester polyols for polyurethanes, thermo-plastic polyurethanes, etc. It is also utilized in natural gas processing as dehydration agents.

1.7.3 TRIETHYLENE GLYCOL

Triethylene glycol, it finds its application in different types of the industry such as cleaning solvent industry, functional fluids industry, absorbent and adsorbent industry, construction material industry, rubber and plastic industry, also in the fabric

industry and automotive industry. It is widely used as a plasticizer for safety glass, separation membranes and molded ceramics.

1.7.4 POLYETHYLENE GLYCOL 400 and 4000

Polyethylene glycols (PEGs), belong to the family of polymers, are the polyether compounds having considerable applications from manufacturing industry to pharmaceutical industry. Because of their low toxicity, they have salient clinical uses. They are exercised as the basis for many laxatives and skin creams [58]. As an electrolyte solvent and separator, PEG is castoff in polymer cells. It is also utilized as a dispersant in toothpastes, as a polar stationary phase in gas chromatography, by integrating with hydrophobic molecules it is practiced in the fabrication of non-ionic surfactants. Another stimulating usage of PEGs is in the preparation of edible films where they act as plasticizers [59]. Erol Ayranci *et al.* used PEGs with varying molecular weights for edible film preparations and their further utilization to foods [60, 61].

1.8 GLYCEROL

Glycerol is a polyhydroxy compound which is widely used in pharmaceutical and food industry as a sweetener and humectant [62-65]. During the process of chemical breakdown of lipids when it reacts with water, in the intestine it falls out as a primary biomolecule as well as in the liver where it takes part in metabolism of glucose [66-68]. Same as water and diols, glycerol also belongs to the family of solvents which contains 3-dimensional grid of hydrogen bonds. Various particular possessions, for instance isobaric thermal expansivity, small isothermal compressibility, high viscosity and relatively large free volume are contributed to the liquid systems by this network [69-73]. In various formulations, glycerol is used as an evaporation regulator and also as a cosolvent in cosmetic and pharmaceutical sciences [74, 75].

1.9 SORBITOL

Sorbitol is one of the sugar alcohol which can be often used in place of sugar in various diet foods (including ice cream and soft drinks), mints, cough syrups, and sugar-free chewing gum [76-78]. Sorbitol contains six OH groups, the reason due to

which hydrogen bond is formed when dissolved with water. In structure of sorbitol, the aldehyde group transforms to a hydroxyl group by the reduction of glucose. Mostly sorbitol is made out of corn syrup, but it can be found in the nature as well, for instance in pears, prunes, apples and peaches. Taking the case of sugar alcohols, the foods comprising sorbitol can generate gastrointestinal distress. It can be utilized as a laxative if consumed as an enema or orally. The drawing of water into large intestine stimulates bowel movements and hence it works as a laxative. Apart from using it as sugar-substitute in reduced sugar foods, sorbitol is also utilized as a soaking agent in cookies and less-moisture foods alike fruit preservatives and peanut butter.

Sorbitol is frequently utilized in advanced cosmetics as a thickener and humectant. It is casted off in toothpaste and mouthwash as well. Due to its high refractive index, some transparent gels can also be formed only with sorbitol.

1.10 STRUCTURE OF WATER

In water (H_2O) molecule, each electron of hydrogen atom is joined with one among six outer shell oxygen's electrons forming covalent hydrogen bonds. In two non-bonding pairs, the four electrons of oxygen are organized. Hence, oxygen atom in H_2O is enclosed by four electron-pairs that usually tend to organize themselves as much as possible, so that repulsions (electrostatic) between pairs of electrons are minimal. This results in a tetrahedral geometry such that the angle amongst electron pairs is 109° . But nonbonding pairs of electrons of oxygen stay closer to the oxygen atom; as such wield tougher revulsion in contradiction to two covalent-bonding pairs. As a result, two atoms of hydrogen are pushed close together. As such tetrahedral geometry is distorted and H-O-H bond angle decreases to 104.5° .

Oxygen is highly electronegative. This implies that the charge distribution due to electron pairs participating in covalent bond between hydrogen and oxygen atoms is not symmetrical. Negative charge density is more near oxygen atom and less near hydrogen atom. This charge displacement constitutes an electrical dipole with positive end on hydrogen atom and negative end at oxygen atom. Thus, we say that due to difference in electro-negativity between hydrogen and oxygen atoms, partial electric charges are developed in water molecule.

1.10.1 Hydrogen bonding

According to Pimental *et al.* [79] a "hydrogen bond exists when a hydrogen atom is bonded to two or more other atoms". Generally, the hydrogen bond refers to the entire group of three or more atoms, which are involved in a configuration X-H-Y, where X and Y may be like or unlike atoms (F, O, N, Cl etc.,). One of the two bonds X-H or H-Y may be stronger (covalent bond) than the other bond (hydrogen bond). The hydrogen bond is often described as a strong electrostatic dipole-dipole interaction. Hydrogen bonding is found with strong electronegative atoms like F, O, N, Cl, etc. Increasing the electro negativity of an atom increases its power of forming hydrogen bonds. In almost all hydrogen bonds the hydrogen atom nearer to one of the two adjacent electronegative atoms than to the other. The change of ultrasonic speeds in solid liquid solutions or liquid mixtures gives an evidence to intermolecular connotation via hydrogen bonding wherever such likelihood occurs.

Partial positive charge on hydrogen atom of one of the molecules of water is electrostatically engrossed by the partial negative charge of the oxygen atom of an adjoining molecule of water. This procedure is known as hydrogen bonding. Hydrogen bond is somewhat longer than O-H covalent bond. Hydrogen bond length is 117pm and O-H covalent bond length is 99pm. This means that hydrogen bond is considerably weak compared to covalent bond. Hydrogen bond is too feeble such that the given hydrogen bond stays not greater than a time fraction of 10^{-9} seconds.

1.10.2. Hydration of ions

Water molecules interact strongly with ions, formed by dissolving electrolytes in water. Owing to high dipole moment of water, the molecules of H₂O nearest to dissolved ions are sturdily linked to it, creating inner or primary hydration sheath. Cations attract negative ends of H₂O molecules. A critical view about the nature of the state of ions and water dipoles in a solution has been envisaged by Bockris [80]. He suggested the term primary hydration should be used during Brownian motion for recognizing the molecules of solvent closer to the ion that have lost translational degrees of freedom and transfer as single entity with ion. Secondary hydration is termed to refer to the solvent molecules not included in the primary hydration shell,

but that undergo significant electrostatic interaction with primary hydration shell. Through hydrogen bonding, organized structure in principal shell generates and a region with the surrounding water get fairly ordered as well.

1.11 THERMODYNAMIC MOLECULAR INTERACTIONS

When a substance is dissolved in another then the properties of the substance change. The interaction study investigates the solubility affected by the chemical nature of both the substances (the solvent and the solute). Generally, a non-ideal behavior of solution is seen when various solute/solvent mixes with another solute/solvent. Many thermodynamic parameters are useful in expressing this deviation from their ideal behavior. Therefore, the information about molecular interactions between different components of liquid mixtures can be significantly obtained through the study of their thermodynamic properties.

The ultrasonic speed along with viscosity and density provides wealth of information regarding nature and strength of molecular interactions. Utilizing density, ultrasonic speed and viscosity data numerous acoustical parameters such as acoustic impedance, intermolecular free length, adiabatic compressibility, internal pressure, Gibb's free energy, relaxation time, ultrasonic attenuation, available volume, molar volume, free volume and enthalpy are computed which delivers evidence about kind of interactions prevailing in the liquid mixtures.

One of the most important factors useful in understanding the structural changes of solutes in solutions is, ion-solvation which includes various ion-solvent interactions. These interactions depend on the nature of solvent, size and structure of ion. Numerous thermodynamic properties like apparent molar volume, partial molar volume, apparent molar isentropic compressibility and partial molar isentropic compressibility depend upon the temperature, pressure and composition and therefore are of great importance in understanding the extent and nature of ion-solvation. The variation in composition and temperature change these properties which can propose several qualitative ideas about solution's behavior in the studied composition range.

The partial molar volume at infinite dilution provides information about solute-solvent interactions. The interactions at infinite dilution, among solute molecules are insignificant and these properties reveal info about interactions among solute molecules and the mixed solvent. Temperature dependence of V_{ϕ}^0 can be more helpful in describing the structural hydration effects as the intrinsic volume of any solute is practically independent of temperature. Likewise, molality dependence of this parameter will be useful in understanding the solute-solute interactions.

Segur and Oberstar (1951) [74] had done the viscometric study in glycerol and its aqueous solutions by using Ostwald's viscometers at different temperatures. The viscosity data was used to calculate viscometric constant and its variation with respect to temperature had been discussed. The viscosity data thus obtained found to be beneficial in design and use of glycerol-handling equipment.

Hammes *et al.* (1966) [81] had examined and determined the acoustical parameters of binary mixtures containing Water-Urea and Water-Urea-Polyethylene Glycol. Ultrasonic velocity measurements were done using ultrasonic interferometer. Density measurements were carried out by the use of Fisher pycnometer. Cannon-Fenske viscometer was used to carry out viscosity measurements. They concluded that when the ultrasonic waves disturb the structure of the liquid the energy losses take place. They also concluded that when the population of unbonded water molecules increase, a little numerical difference occurs between isothermal and adiabatic compressibilities in the aqueous solution. They concluded that with the increase in the urea concentrations there is a variation in the temperature dependence of the viscosity.

Morenas and Douheret (1978) [45] studied the thermodynamic behavior of few glycol and water mixtures by analyzing the excess and partial molar properties of the mixtures. The density of pure glycols and binary mixtures was calculated by Y-shaped pycnometer in a thermostat water bath at temperatures 288.15 K, 298.15 K and 308.15 K. Using densities of pure liquids and liquid mixtures, partial molar volumes and excess molar volumes were evaluated. The deviations from ideal mixing volumes were found to be negative and trend was increasing with respect to ether functions present in the molecule. The dependence of excess values on temperature had also been observed for monoethylene glycol-water mixtures. An extremum in water-rich region revealed by the values of partial molar volumes for all the liquid mixtures.

Bohne *et al.* (1984) [82] reported the thermo-physical properties such as thermal conductivity, density and viscosity for the binary mixtures of ethylene glycol and water. A concentric cylinder device, a digital density meter and Ubbelohde viscometer were used to measure thermal conductivity, density and viscosity. Prandtl-numbers were

calculated using measured experimental data. By using various theoretical models, the experimental results are verified.

Bagchi *et al.* (1986) [83] had examined and determined the investigation on the viscometric and ultrasonic properties in the binary mixture of the ISRO polyol with polypropylene glycol. Ultrasonic interferometer at 2MHz was used for the ultrasonic velocity measurements. Density determination was carried out by using pycnometer. For the viscosity measurements Ubbelohde viscometer was used. The studies conducted concluded that with solvents the ISRO polyol happens to be solvated. They also concluded that ISRO polyol shows interactions with polypropylene glycol.

Hout *et al.* (1988) [84] had carried out the thermodynamic study for the mixtures of water and ethylene glycol at temperature 5, 25 and 45⁰ C. The density of the solutions was measured using flow densimeter and isobaric heat capacities per unit volume by micro calorimeter. The experimental values were further used to calculate excess molar properties, apparent molar and partial molar properties. The negative excess values were found in the systems due to negative effect of hydroxyl group and positive contribution of methylene group. The magnitude of excess enthalpies showed that exothermic mixing of water-ethylene glycol was significantly conquered by interactions including the hydroxyl group of ethylene glycol. The continuous change in various higher order thermodynamic properties was observed in leu of increasing connectivity among ethylene glycol molecules.

Mehrotra *et al.* (1989) [85] had determined the acoustical and thermodynamic parameters of calcium soap solutions at various temperatures, the conductance of the solutions was determined by using digital conductivity meter. Ultrasonic interferometer working at 4MHz frequency was used to carry out the ultrasonic velocity measurements. Their results suggest that the soaps act as weak electrolytes in dilute solutions. They also concluded that when the temperature increases the CMC values also increase. Their results concluded that when the soap concentration increases there is a reduction in the L_f , solvation number, compressibility, and adiabatic compressibility

(β) and simultaneously there is an increase in the molar sound velocity, ultrasonic velocity, apparent molal compressibility and specific acoustic impedance.

Rao *et al.* (1989) [86] had examined the acoustical parameters of mixtures of polyvinyl pyrrolidone with N, N-dimethyl formamide solutions. Pycnometer was used for the density measurements. For viscosity measurements Ostwald's viscometer was used. Studies of refractive index, viscosity and ultrasonic velocity on PVP-DMF solutions showed the existence of solvent-solute interaction.

Lee and Hong (1990) [87] reported excess molar volumes for the binary and ternary mixtures of ethylene glycol, methanol and water. The densities of four systems (ethylene glycol + methanol, ethylene glycol + water, methanol + water and ethylene glycol + methanol + water) were measured using Anton Paar DMA at temperatures 283.15, 293.15 and 303.15 K. From the density data, excess molar volumes were calculated and the values were found to be negative for all three binary systems and one ternary system. To check the composition dependency, the Redlich-Kister equation was used and A, B coefficients were computed by least square method.

Douheret *et al.* (1991) [88] measured densities, isobaric heat capacities and ultrasonic speeds for the binary mixtures of ethylene glycol and water at different temperatures. Density and ultrasonic speed measurements were then used to compute excess molar volume and isentropic compressibility. Isobaric and isentropic expansivities were also derived from the results. A segmented-composition model was used to analyze the obtained excess molar quantities. The obtained results suggested highly labile clusters with a very diffident degree of hydrophobic aggregation.

Kamugai *et al.* (1993) [89] had reported the density and viscosity of different binary mixtures of HFC-134a with glycols mixtures in temperature ranging from 273K to 333K. Rolling-ball viscometer was used to calculate the viscosity which was plotted with standard liquids of viscosities and densities. Also, by using glass-pycnometer density was calculated. For viscosity less than 3.4% of uncertainties of measurement were observed while it was 0.4% for density. Due to the reason that HFC-134a has a

limited miscibility for glycols so it decreases with the decrease in the molecular weight of glycols. As the weight fraction of HFC-134a increases the viscosity of all the mixtures decreases considerably.

Reddy *et al.* (1994) [90] had investigated viscosity, ultrasonic speed and excess volume data for aqueous binary solutions of ethylene glycol, 2-ethoxyethanol, 2-methoxyethanol and 2-butoxyethanol at temperature 308.15 K. The values of k_s and density were evaluated from the obtained results of computed data. The values are coming positive for the viscosity deviations whereas coming negative for excess volume deviations. The incoming results are explained in terms of interactions occurring between like and unlike components.

Pal *et al.* (1994) [91] calculated excess and apparent molar properties of water + PEG mixtures at different temperatures. The whole composition range containing the values of excess molar volumes were found to be all negative and through this data apparent molar volumes have been calculated. It can be concluded from the results that in the water-rich region weak-hydrophobic effects might develop although its extent rises with the size of the hydrocarbon chain. The entire composition range of water-glycol systems provided the densities obtained from the excess volume measurements and from the densities the apparent molar volumes were calculated.

Aminabhavi and Gopalakrishna (1995) [39] reported the viscosity, ultrasonic velocity, density, and refractive index in the aqueous solution of various liquids at temperature 298.15K. The excess molar volume, deviations in viscosity, speed of sound, molar refractivity and isentropic compressibility have been calculated from these results.

Rajulu and Sab (1995) [92] had examined and determined the various parameters of binary mixtures of polyethylene glycol at 30°C with water. At 65°C the chemicals were dehydrated under vacuum. Variable path interferometer at 2MHz was used to determine the ultrasonic velocity. Density bottle was used to determine the density. Their results

showed a non-linear relation showing the existence of a relationship between PEG and water.

Magazu *et al.* (1996) [93] had examined the acoustic properties of α , α -trehalose with water solutions. Ultrasonic interferometer was used at a frequency of 3MHz to carry out the ultrasonic velocity measurements. Pycnometer was used for the density measurements. Their data concluded that there are structural changes that occur in these solutions and even the mixing process is not idealistic. They also determined the temperature dependence and hydration number of trehalose.

Pal and Singh (1997) [94] calculated the velocity and viscosities of water + glycol mixtures at temperatures 303.15K and 308.15K. In order to obtain isentropic (adiabatic) compressibility the results of for additional molar volumes are combined with the previous results.

Tsierkezos and Molinou (1998) [46] calculated the properties of water + EG at the different range of temperatures and the results obtained from this are fitted into the R-K equation to derive the corresponding parameters. The values of the properties are all negative and they show a minimum at the same water-rich region of the solution. The excess volumes are found to be negative for all the mixtures between water and ethylene glycol. Also, it is observed that the viscosity deviation values for all the range of temperatures are negative and they increase with rise in temperature. The refractive index deviations are reported to be negative for all the range of mixtures.

Kirincic and Klofutar (1998) [95] determined the densities of some aqueous of some PEG at temperature 298.15K. The partial specific volume of the solvent and solute and the apparent specific volume of the solute were calculated from these data. It was found that with the decrease in the partial specific volume of the solute, the concentration increases. In contrast to this, the partial specific volume of the water increases with rise in the concentration of the solute very marginally.

Ali et al. (1998) [96] had examined and determined the molecular interaction studies on acetonitrile, ethanol, 1-hexanol, 1-octanol, N,N-dimethylformamide, on ethanol with 1-hexanol and 1-octanol and on acetonitrile with N,N-dimethylformamide at 303.15K. dry box was used to prepare all the solutions. Cannon-Ubbelohde viscometer was used for viscosity measurements. Ultrasonic velocity measurements were carried out by ultrasonic interferometer working at frequency 3MHz. they concluded that with the increase in the strength of molecular interaction, the excess β and the excess free length happen to be increasingly negative.

Henni et al. (1999) [97] reported the experimental data for the viscosity and density of triethylene glycol monomethyl ether. Studies of Helper (1969) suggested that on addition of water to TEGMME does not affect its structure and Grunberg-Nissan were also calculated and were found to be positive.

Geyer et al. (2000) [98] measured the densities and V^E of the binary mixtures of (glycol + H₂O) at constant atmospheric pressure and various temperatures. The V^E values of all the solutions are negative for all the different range of temperatures. Results obtained were compared to the polynomial equation of Redlich and Kister. For results related to the temperature dependence density was measured for pure glycols and (glycol + water) in this study.

Huang and Nishinari (2001) [99] used the differential scanning calorimetry (DSC) to study the interaction between PEG and H₂O. With increase in the molecular weight the eutectic point composition shifted to lower concentration of PEG and the eutectic point temperature shifted to higher temperatures.

Banipal et al. (2001) [66] calculated the V_{ϕ}^0 of transfer at 25 °C of some amino acids from H₂O to aqueous glycerol solutions from the solution densities by using vibrating-tube digital densitometer and the transfer volumes from water to different glycerol-water mixtures are obtained from the calculated partial molar volumes at infinite solution. Using McMillan-Mayer method the interaction coefficients are obtained. To conclude,

the transfer volumes of amino acids in aqueous solutions of t-butanol and glycerol behave in the similar way.

Branca *et al.* (2002) [100] studied the change of solution viscosity w.r.t solute concentration and from ultrasonic velocity measurements and reported the hydration numbers. As the degree of polymerization increases the hydration numbers which are calculated from both viscosity and acoustic data also increase quickly. Also it was found from the acoustic data that if there is increase in temperature then the polymer-water interaction strength decreases which results in the loss of water molecules which are not tightly bonded.

Vergara *et al.* (2002) [101] investigated polymeric solutions with the inverted K-B theory which emphasized basically on the significance of the molecular size on the preferential solvation analysis by carefully analyzing the aqueous solution of the solutes belonging to the PEG homologous series and the most important result which was found is that the only positive preferential solvation is between PEG and H₂O.

Sastry and Patel (2003) [102] calculated the relative permittivities, densities, viscosities and ultrasonic velocity of alkyl acetates + glycols at different temperature. All these deviation functions are fitted to a Redlich-Kister type equation. By collision factor theory the values of speeds of sounds in these mixtures are calculated.

Sun and Teja (2003) [103] measured the densities, viscosities and thermal conductivities of aqueous EG, DEG and TEG mixtures at temperatures range from 290K to 450K with the concentration of glycol from 25 to 100 mol %. The excess properties were studied for the temperature behavior.

Lourdin *et al.* (2003) [104] studied the density of starch-water systems which has concluded that the volume changes are comparable to physical ageing when the components are mixed. Maltose and starch have strong attraction for low-molecular weight polar molecular like water and glycerol which brings the negative volume

change. Antiparticipation phenomenon which was previously observed in the starch systems was found to be in one-to-one correspondence with this volume change.

Yang *et al.* (2003) [105] calculated the viscosities and densities for aqueous EG mixtures at various temperature. At lower temperatures for the entire composition, the excess volumes are negative. Although they exhibit S-shaped concentration dependence at higher temperatures.

Fujisawa *et al.* (2004) [106] calculated the heat capacities of 1,2 Alkanediols in dilute aqueous solutions at various temperature by using DSC. Another thing which was determined was heat capacity changes by dissolution of alkanediols so for 1,2-ethanediol or 1,2-propanediol it increased with increase in temperature whereas for 1,2-butanediol the heat capacity changes decreased with temperature increase. To conclude, the dissolution of 1,2-butanediol were found out to be different from the other two alkanediols.

Valtz *et al.* (2004) [107] reported the liquid densities and V^E for the binary H_2O + diethylene glycolamine, and H_2O , methanol, ethanol, 1-propanol + TEG systems at different temperature. For all the systems that were investigated the V^E were found to be negative. Molar excess volume increase with temperature water containing systems whereas for alcoholic systems the decrease was observed i.e molar excess volumes became more negative with temperature increase. At constant temperature the absolute value of V^E for triethylene glycol systems decrease in the order: H_2O > methanol > ethanol > 1-propanol. Three parameter Redlich-Krister equation was used to compare the experimental results.

Tasic and Klofutar (2004) [108] had investigated apparent specific refraction and apparent specific volume of poly (oxyethylene) glycols in the solution of benzene and 1,4 Dioxane at 298.15 K temperature. The void V_ϕ^0 and intrinsic volume of molecules of solute were utilized to analyze volumetric data. It was found that both partial molar refraction and V_ϕ^0 depends linearly on oxyethylene group and are additive in nature.

Sommer *et al.* (2004) [109] had measured apparent specific volume of aqueous solutions of poly (ethylene oxide), poly (butylene oxide), poly (propylene oxide) and octadecyl chains in the micellar state from apparent specific densities values with respect to temperature ranging from 10 to 90⁰C with the help of vibrating tube densimeter. The NMR spectroscopy was employed to check the composition of block copolymers. The obtained results were compared with the already published data.

Syal *et al.* (2005) [110] studies the sound velocity, density and viscosity on solutions of PEG with molecular weights (8,000 – 11,000) and (20,000) in water and its binary mixtures with Acetonitrile (AN) at 25⁰C. Various parameters such as acoustic impedance (Z), adiabatic compressibility (β), intermolecular length, relative association, molar sound velocity, solvation number (S_n), apparent molar adiabatic compressibility (ϕ_{ks}), viscous relaxation time, internal pressure (I) and free volume (V_f) were calculated from the velocity, density and viscosity data values.

Rao *et al.* (2005) [111] had examined and determined the ultrasonic velocities for liquids mixtures of o-chlorophenol with ethylbenzoate, anisicaldehyde and acetonitrile at four temperatures 303.15, 308.15, 313.15 and 318.15K. They redistilled and purified o-chlorophenol, anisicaldehyde and acetonitrile. Liquid mixtures of different composition were made by mixing pure liquids in cleaned and dried flasks. With interferometer at a frequency of 1MHz ultrasonic velocity of three binary liquids were measured.

Zwirbla *et al.* (2005) [112] had done ultrasonic studies of water mixtures with EG, PEG-200 and PEG-400 at different temperatures. The obtained experimental data had been employed to compute adiabatic Compressibilities by using Laplace equation. The variation of values of adiabatic Compressibilities with respect to concentration and temperature had also been investigated. The formation of Pseudo-stable molecular structure and structural interactions had been observed at low ethylene glycol and polyethylene glycols concentrations.

Hu *et al.* (2006) [113] measured the densities and viscosities for the quaternary system mannitol + sorbitol + sucrose + water and its binary and ternary subsystems at temperature 298.15K. The results that were obtained were used to test the applicability of simple equations for the density. The anticipated results were found out to be good when compared with measure values which concluded that that density, kinematic viscosity and viscosity of multicomponent nonelectrolyte solution which obey the linear isopiestic relation.

Raman *et al.* (2007) [114] studied the variations of D -mannitol in water at different temperatures and concentrations using ultrasonic velocity measurement. The basic acoustical parameters give important evidence to know the solvent-solvent interactions in the aqueous solutions. With the increase in temperature there is a constant reduction in the internal pressure, shear relaxation time and classical sound absorption. The hydration number is found out to be 8 through this study.

Ali *et al.* (2007) [115] measured the density, viscosity and refractive index behaviour of amino acids in aqueous glycerol at different range of temperatures. Through these experimental data the apparent volumes of transfer, the infinite dilution apparent molar volumes, the partial molar volumes of transfer were calculated

Blodgett *et al.* (2007) [116] reported the V_ϕ and apparent molar heat capacities for adonitol, dulcitol, glycerol, meso-erythritol, myo-inositol, D-sorbitol and xylitol at different temperature and the pressure 0.35 MPa. Values of V_ϕ and apparent molar heat capacities for the sugar alcohols are compared to one another.

Kumar and Rao (2007) [117] had studied the molecular interaction and ultrasonic velocity of mixtures containing alkanols with aqueous propylene glycol. With a variable path interferometer working at 2MHz the ultrasonic velocity was measured. They determined the wavelength of ultrasonic wave at the working frequency. They concluded that the difference of ultrasound velocity with molefraction of methanol and ethanol is monotonic.

Kushare *et al.* (2007) [118] had reported the density and ultrasonic velocity data for polyethylene glycols (PEG-400, PEG-1000 and PEG-4000) in solutions of methanol, H₂O and benzene from (0.05 to 0.5) mol·kg⁻¹ molality at T = 298.15 K. The obtained data was used to calculate V_ϕ , apparent molar isentropic compressibility and adiabatic compressibility for molecules of solute in all solvent medium. The partial molar properties were employed to investigate transfer volume and transfer compressibility for polyethylene glycols from methanol to water and benzene to water medium. Shio's method was applied to compute the hydration number of solute molecules and it was found that polyethylene glycol-4000 show maximum hydration.

Zhang *et al.* (2008) [119] studied the density and V^E of EG and H₂O to demonstrate hydrogen bonding interactions. It was observed that the density analysis of ethylene glycol and water mixture was displayed at above 0.4 (molar fraction). Strong hydrogen bonding interactions of water hydrogen atoms with hydroxyl oxygen atoms in ethylene glycol were observed.

Raman *et al.* (2008) [120] detailed study of glycerol in H₂O has been observed at different concentrations and various temperatures using speed of ultrasonic waves. Constant decrease was observed in the classical sound absorption and shear relaxation time with the rise in temperature which indicates the inter-molecular forces due to thermal agitation of the molecules at high temperatures. This study indicates that the hydration number is 4.

Sastry *et al.* (2008) [121] measured the thermophysical properties for DEG + nitrobenzene and TEG + (chloro, bromo, nitro) benzene systems at atmospheric pressure and temperature range from 298.15 to 313.15 K. The V^E obtained are fitted into the Redlich-Kister equation. It was found out from the qualitative analysis of excess molar volumes that the structure-making effects are predominant in these mixtures.

Garcia *et al.* (2008) [122] recorded the liquid densities and viscosities for aqueous solutions of DEG at the temperature range from 283.15 K to 353.15 K. Vibrating tube

densimeter is used to calculate the density whereas viscosity is measured using the Cannon-Fenske viscosimeters. Negative deviations are observed for excess molar volumes at all the range of temperatures and it is found that it becomes more negative with decrease in temperature. Between the temperature range investigated the viscosity deviation changes its sign from negative to positive in the water-rich region.

Ayranci and Sahin (2008) [123] had investigated the molecular interactions of ethylene glycol, polyethylene glycols at three temperature $T = (288.15, 298.15$ and $308.15)$ K. The experimentally obtained data of densities and sound velocities was used to evaluate V_ϕ and $K_{\phi,s}$. The investigation was done on the variation of V_ϕ^0 and $K_{\phi,s}^0$ with temperature and number of repeating unit in polyethylene glycols. Group additivity approach was utilized to compare the experimental data with the literature data. The outcomes were described in terms of conformational effects and hydration of polyethylene glycols in water

Tsierkezos and Palaiologou (2008) [124] measured the densities, ultrasonic velocity and k_s of either H₂O or DMSO with EG, DEG, TrEG, TetrEG, PG and BG at temperature 298.15 K. The values thus calculated were compared to the Redlich-Kister equation. Glycol molecules are likely to create specific interactions through formation of hydrogen bond with either H₂O or DMSO molecules.

Kinart *et al.* (2009) [57] calculated the densities and relative permittivities of binary mixtures of 2-ethoxyethanol with EG, TEG and tetraethylene glycol at different temperatures. The V^E and deviations in relative permittivity have been calculated. It was found that the values of V^E become more negative with the rise in the chain length of glycol molecules.

Palani *et al.* (2009) [125] had examined and determined the thermodynamic and acoustical studies in aqueous solutions at temperatures- 303K, 3038K and 313K. All the chemicals were used without purification. Specific gravity bottle was used to carry out the density measurements. Viscosity measurements were carried out by the Ostwald's viscometer. Velocity measurements were carried out by the ultrasonic

interferometer at 3MHz. They concluded that the existence of the strong molecular interaction is revealed through the results of excess properties which is touted due to the supremacy of the charge transfer and hydrogen bonding between the mixture components. They also concluded that due to the existence of the thermal dispersion forces and weak intermolecular forces when the temperature increases the interaction strength is likely to become weak.

Patil *et al.* (2010) [126] had investigated the interaction of molecules in the binary liquid mixtures of 1- heptanol and 1- hexanol with nitrobenzene. Density determination was done at temperatures 303.15 and 313.15K. Stopper measuring flasks were used to prepare the binary liquid mixtures of different compositions. Bi-capillary pycnometer was used to measure the density. Viscosity was measured by an Ubbelohde viscometer. By ultrasonic interferometer the ultrasonic velocity was measured at frequency 2MHz. With the increase in the chain length the self-association of the alkanols decrease. The decrease in the electron densities is due to the presence of an electron withdrawing group on benzene.

Dandwate (2010) [127] had examined and determined the ultrasonic velocities of dimethyl sulphoxide with methanol, ethanol and propanol. Different techniques such as pulse method, acousto-optical method and ultrasonic interferometer were used to measure the ultrasonic velocities. The measurements were carried out at 25°C. Specific gravity bottle was used for the density measurements. It was concluded that when the density of the binary mixture decreases there is a decrease in the velocity of the ultrasonic waves. It had been observed that the bulk modulus is highest in case of the dimethyl sulphoxide and lowest in case of methanol.

Anbarasu *et al.* (2010) [128] had determined the densities and ultrasonic velocities of the mixtures containing ethyl acetate and 2-butanone at different mole fractions. Molecular interactions were studied with ultrasonic measurements using interferometer method. Bicapillary pycnometer was used to measure the densities. Single pan digital balance was used to measure the weights. Airtight glass bottles were used for preparing mixtures. Variable path ultrasonic interferometer was used to determine the sound

velocity. They confirmed the observations of the excess molar volume (V^E) by FTIR spectrum.

Dubey *et al.* (2010) [129] reported the densities, speed of sounds and viscosities for the whole range for the binary mixtures of DEG monomethyl ether (DEGMME) with 1-alkanols at different temperature. Through these experimental values, V^E , deviances in viscosity, k_s , deviations in k_s and deviations in sound velocity are measured.

Egorov *et al.* (2010) [130] calculated the density of water-ethylene glycol mixtures using vibration densimeter at the temperature range 278.15 K to 333.15 K and at atmospheric pressure. It was observed that the density of the mixture increased with increase in EG concentration at all temperatures. Also, the values of V^E for all temperature were found to be negative.

Egorov *et al.* (2010) [131] reported the densities and compressibility coefficients of EG + dimethylsulfoxide mixtures at the temperature range from (278.15 to 321.15) K. It was observed that the values of excess molar volumes reduce with reducing pressure and temperature. Pressure and temperature is strongly related to the association processes in the ethylene glycol + dimethylsulfoxide mixture as on low pressures, with increase in temperature contributes to association processes but at high pressure it does not.

Guignon *et al.* (2010) [132] studied the volumetric properties of different pressure-transmitting fluids (PTF) and compared them with those of water. Castor oil, silicon oil, PG, EG and ethanol specific volumes were calculated at different temperature both individually and in a mixture with water or ethanol. The observed behavior of the pressure and temperature for all the volumetric properties of PTFs were different from that of water.

Zhu *et al.* (2010) [133] calculated the densities and viscosities of sugar alcohol aqueous solutions at temperature range of (293.15, 303.15, 313.15, and 323.15) K. The data values for viscosities are correlated using exponential model with the maximum

average deviation of 3.7%. Also, it was found out the temperature or concentration show a linear relation with the values calculated for densities and the data values for densities were correlated using linear equation.

Begum *et al.* (2011) [134] measured the densities, viscosities and surface tension of the system water + DEG at temperature range from 283.15 K to 303.15 K. From the measure values of densities, the V^E were calculated. Polynomial equation was used to fit in the densities, viscosities and surface tensions add Redlich-Kister equation was used to fit in the V^E .

Koohyar *et al.* (2011) [135] calculated the viscosities, densities at temperatures (303.15, 308.15, 313.15, 318.15 and 323.15) K and the refractive indices at same temperatures for (L-cysteine hydrochloride monohydrate [LCHCMH] + D-sorbitol + water) and (glycerol + D-sorbitol + water). Change of refractive indices were calculated from refractive indices. It was observed that the calculated quantities are positive when there is change of refractive index in mixing.

Thirumaran *et al.* (2011) [136] had acoustical investigation of liquid mixtures of DMSO with aromatic hydrocarbons at 303.15K. The studies were carried out in a broader way as DMSO has its utilisations in the medicine world. DMSO can easily penetrate biological membranes, facilitates chemical transport into biological tissue. To make solutions they used the water which was deionised, distilled and degassed. For velocity measurements, ultrasonic interferometer with frequency 2MHz was used.

Ubagaramary *et al.* (2012) [137] had examined and determined the molecular interaction of binary mixture of IBMK with carbonyl molecules. Viscosity measurements were done by the Ostwald's Viscometer. Ultrasonic interferometer at 2MHz was used to carry out velocity measurements. They concluded that the calculated acoustical parameters showed the presence of the molecular interaction in IBMK +Cyclohexanone, IBMK + Methylsalicylate to acetophenone+ Chlorobenzene. This concluded the strong H bonding and strong Dipole-Dipole interactions in between the molecules.

Ramteke (2012) [138] had measured the ultrasonic velocity of liquid mixture containing alpha-picolin in ethanol at different temperature. The densities of the pure components and binary mixtures were measured by hydrostatic sinker method. They gave special attention to avoid the vaporisation of solution. They prepared the mixtures of different concentrations in mole fraction. The temperature was maintained constant using thermostat for pure liquids and their mixture. Over the whole concentration the acoustic data of viscosity, speed of sound, and density other thermodynamic parameters, they suggested the existence of a strong molecular interaction in the binary liquid mixture.

Bhandakkar (2012) [139] had studied the interaction of liquid mixture containing methyl methacrylate (MM) using ultrasonic technique. viscosity, speed of sound, and density for the binary systems of methyl methacrylate + methanol, methyl methacrylate + p-dioxane, and methyl methacrylate + cyclohexane at the temperature 303K have been examined. Hydrostatic sinker method in the temperature range of 10-40°C was used. By employing the ultrasonic time inter-velometer, the ultrasonic velocity of frequency 10MHz and density for the binary mixtures were measured. The viscosity, density and ultrasonic velocity were used to study the molecular interaction present in the methyl methacrylate with methanol, dioxane and cyclohexane. Gibb's free energy calculations were used to estimate polymer solvent interactions parameters. They concluded that there is a presence of higher degree of molecular interaction between methyl methacrylate and methanol and this is due to the hydrogen bonding in the binary liquid mixtures.

Pathak *et al.* (2012) [140] had examined and determined the thermodynamic parameters and ultrasonic velocity of the mixture of Epoxy resin solutions based on cardo symmetric double schiff bases at temperature 308.15K. Gel permeation chromatography was used to determine the molecular weights. Density measurements were carried out by using specific gravity bottles. Ubbelohde viscometer was used for viscosity measurements. Ultrasonic interferometer at 2MHz was used to carry out the velocity measurements. They concluded the presence of strong molecular interaction in

the solutions is indicated due to the non-linear or linear decrease or increase of thermodynamic parameters.

Parveen *et al.* (2012) [141] had examined and determined the molecular interaction of aniline with carboxylic acid at temperatures of 293.15K, 303.15K and 313.15K. Glass stoppered weighing bottles were used to prepare the mixtures. Density measurements were carried out by using pycnometer. Brookfield LVDV-II+Pro Programmable viscometer was used for viscosity measurements. They concluded the presence of complexes by intermolecular H-bonding between carboxylic acid and aniline through the studies of refractive index, ultrasonic velocity, viscosity and density measurements. They also concluded that different non-linear and thermo acoustical parameters provide a suitable means for explicating liquid state properties associating to sound propagation data.

Egorov and Markarov (2012) [142] used vibrating tube densimeter to calculate the densities of ethylene glycol and tetra-butanol liquid mixture at temperature range between 278.15 K and 348.15 K. It was found out that with the growth of tetra-butanol concentration there is an increase in the specific volume of the mixture. V^E were calculated and were found to be negative at all temperatures but deviates from ideality with rise in temperature. V_ϕ^0 of EG was also calculated and was found to be decreasing with increase in tetra-butanol concentration whereas partial molar volumes increased at all temperatures for tetra-butanol.

Egorov and Markarov (2012) [143] measure the densities of glycerol + tetrabutanol from the temperature range of 293.15 K to 348.15 K using the vibrating tube densimeter. The V^E were calculated and found to be negative at all the temperatures over the entire temperature range. V_ϕ^0 were also measured and was found to be decreasing with increase tetra-butanol concentration.

Katrinak *et al.* (2012) [144] had measured the density and speed of sound data for three polyhydric alcohols that derived from propane (propane-1,2-diol, propane-1,3-diol, propane-1,2,3-triol) in water at infinite dilution with the help of DSA 5000

vibrating tube densimeter and sound analyzer at $T = (278 \text{ to } 318) \text{ K}$ temperatures and atmospheric pressure. The measured data of density and ultrasonic speed had been utilized to investigate standard molar volume and standard molar isentropic compression of aqueous solution of three polyhydric alcohols which derived from propane.

Egorov *et al.* (2013) [145] calculated the coefficient of compressibility for the (water + ethylene glycol) binary mixture at the temperature range from 278.15 K to 323.15 K and at pressures from 0.1 to 100 MPa. Molar volumes were also calculated and was found out to be negative at all temperatures and it decreased with decrease in temperature. Increase in the pressure growth leads to the decrease in the limiting partial volumes of water and EG. New hydrogen bonds formation leads to the ordering of the mixture compression.

Begum *et al.* (2013) [146] measured the densities and viscosities for water + triethylene glycol, water + tetraethylene glycol and water + tetraethylene glycol dimethyl ether at different temperatures. Surface tensions were also measure for these systems at 303.15 K for different mole fractions. Density and viscosity decrease gradually with increase in the concentration of glycols. Also, the surface tensions for aqueous solutions of methyl-substituted glycols were observed to be lower than the other aqueous glycols.

Pal *et al.* (2013) [147] calculated the densities and speed of sounds for binary mixtures of 1,4-dioxane with propanol and butanol isomers using an DSA 5000 at different temperatures. V^E was also observed from the experimental. Excess isentropic compressibility was also measured and it was observed that the values are negative over whole mole fraction range at all temperatures.

Jiang *et al.* (2013) [148] measured the density and viscosity of sorbitol/maltitol in L-ascorbic acid aqueous solutions at temperature range from 293.15 K to 323.15 K. It was observed that the densities and viscosities of sorbitol/maltitol in in L-ascorbic acid aqueous solutions increase monotonously with the molality of solute (sorbitol or maltitol) and the molality of L-ascorbic acid however it decreases with the increase in

temperature. The limiting partial molar volume and limiting partial molar volume of transfer were calculated through experimental values of densities.

Pal *et al.* (2013) [149] calculated the densities and ultrasonic velocity for binary mixtures of dipropylene glycol dimethyl ether with n-alkyl esters and from which V^E and k_s are also measured. At negative values of all the mixtures V^E was observed to contract. Using Jouyben-Acree model the observed densities and ultrasonic velocity were compared and results thus produced were found to be accurate.

Sastry *et al.* (2013) [150] reported the density and ultrasonic velocity for the binary mixtures of methyl benzoate at temperature range (303, 308, 313, 318 and 323) K. From the experimental data V^E and k_s is calculated. The V^E is found to be negative mostly for 1-propanol but it becomes positive as the alcohol chain increases where excess values of k_s are found to be negative over the whole range and at all the temperatures. With the rise in chain length of alcohol in the binary mixtures the strength of interaction decreases.

Zemankova *et al.* (2013) [151] calculated the excess volumes and excess heat capacities for alkanediol + water systems in the temperature range from 283.15 K to 313.15 K. Excess volumes are observed to be negative over the whole range and they become less negative as temperature increases whereas excess isobaric molar heat capacity stays positive mostly, although it becomes negative for few mixtures at several compositions and temperatures. As far as temperature is concerned excess isobaric molar heat capacity rise with rise in temperature.

Pal *et al.* (2013) [152] ultrasonic velocities and densities of molecular interactions in n-Alkoxypropanols with n-alkyl ester mixtures at temperature range from 288.15 K and 308.15 K. V^E and deviations in isentropic compressibility have been computed from the experimental values. The deviations in k_s is observed to be positive over the whole range and the magnitude decrease with increase in the size of polar group of alkoxypropanols. Moreover, with decrease in the chain length of ester the values in k_s increases.

Kumar *et al.* (2013) [153] calculated the densities and sound velocity for binary liquid mixtures of alkoxypropanol with branched alkanols at temperature range of (288.15, 298.15 and 308.15) K using an Anton-Paar DSA 5000M densimeter. From the experimental data excess molar volumes and deviations in isentropic compressibilities have also been calculated. The results thus obtained are compared with the results observed earlier.

Sannaningannavar *et al.* (2013) [154] had examined and determined the thermoacoustical parameters of the mixtures of polyethylene glycol-400 at 299K and 363K. Ultrasonic interferometer at 3MHz was used to carry out the velocity measurements. By using pycnometer, the density measurements were carried out. Electronically regulated thermostatic water bath was to maintain the temperature. They concluded that when the temperature is increased PEG-400 goes under volume expansion. They also concluded that the structure becomes distorted when the temperature is raised. They also concluded that when the intermolecular forces are decreased the chain and unfolding expansions take place with the rise in the temperature. They also showed the temperature dependence of the elastic and inertial properties of the sample.

Pal *et al.* (2013) [155] had examined the volumetric and acoustical study of liquid mixtures containing dipropylene glycol dimethyl ether with methyl acetate, ether acetate and n-butyle acetate in the different temperature range. They calibrated the apparatus with heptanes, hexane, octane, cyclohexane and benzene before conducting measurements. Thermodynamic parameters were calculated with the experimentally calculated values. They found the mixtures to be contracting due to negative values of the molar volume and also found the mixtures to be of greater compressibility than the pure components.

Kaur *et al.* (2013) [156] had investigated the acoustic parameter of the mixture containing polyvinyl acetate with acetic acid with ultrasonic technique. The samples were investigated without purification (purity= 99%). They prepared the solution by dissolving the polyvinyl acetate in a fixed volume of the acetic acid. Electronic balance

was used to weigh the samples. With a variable path interferometer working at 2MHz the ultrasonic velocity was measured. The standard liquid used was distilled water. All the measurements were made at the room temperature. They concluded that the ultrasonic velocity rises and the density rises with the rise in the concentration. They concluded with these results that a large number of molecules are responsible for transmitting energy which results in the increase in the ultrasonic velocity.

Pal *et al.* (2013) [157] has investigated the ultrasonic velocity and density for binary mixtures of 1,4-dioxane with propanol and butanol isomers at different temperatures. Built-in solid-state thermostat was used to control the density and sound as they are extremely responsive to temperature. Airtight stoppered glass bottle to avoid evaporation was used to keep the mixtures prepared. Molar volume and k_s were obtained using the density and speed of sound. They concluded that with the rise in the temperature and alkyl chain length for both 1-alkanol and 2-alkanol there is a rise in the magnitude of the V^E . They discussed all the properties in terms of molecular interaction.

Bhavani *et al.* (2013) [158] evaluated theoretically the speed of the sound in binary liquid mixtures at different temperatures. The chemicals were used without purification (purity=99%). By using the thermostatically controlled water bath, the temperature was maintained constant. Specific-gravity bottles were used to measure the density. Electronic balance was used to measure the weights of the mixtures.

Hnedkovsky *et al.* (2013) [159] determined ultrasonic speed and density of dilute aqueous solutions of alkane- α , ω -diols at different temperatures. Standard molar volumes and standard molar isentropic compressions were calculated. They discussed the relations of the given standard parameters to the ratio of hydrophilic and hydrophobic parts of solute.

Moattar and Tohidifar (2013) [160] had studied the temperature effect on transport and volumetric properties of aqueous solutions of poly ethylene glycol di-methyl ether 2000 + polyethylene glycol 400 at $T = (293.15 \text{ to } 313.15) \text{ K}$ temperatures. The modified

Wilson model for polymer solution was employed to find V^E , excess molar isentropic compression, deviation of viscous flow and excess Gibb's free energy of activation of viscous flow that obtained from experimental density, speed of sound and viscosity data. At dilute range data for density was utilized to compute apparent specific volume at infinite dilution which further provides the information about segment-segment and segment-solvent interactions.

Adam *et al.* (2014) [161] measured the densities of aqueous solutions of ethylene glycols at temperature range from 293.15 K to 318.15 K. Volumes of all mixtures observed at a constant temperature was found out to be linearly dependent on solute molality, from these results the V_ϕ^0 were also calculated for all the solutes. The partial molar volumes thus obtained was found to be increasing slightly with increase in temperature. Further, the thermal expansion coefficients were also calculated for all the solutes and was observed to be increasing with increase in temperature and molality.

Kumar *et al.* (2014) [162] had investigated the interaction of amino acid in aqueous triammonium citrate solutions at different temperatures. By using Sartorius balance all the weightings were made. Viscosities were measured by Anton Paar Automated Micro Viscometer (AMV). Peltier thermostat was used to control the temperature. From their earlier reported results, the densities were taken. They concluded that with the increase in the amino acid concentration there is an increase in the viscosity. B-coefficients and analysis of the viscosity were obtained through experimental data. Their results obtained from the viscosity measurement are supported by the volumetric data.

Dash *et al.* (2014) [9] had determined the ultrasonic studies on molecular interaction in ternary liquid mixture of dimethyl acetamide at different frequencies at different mole fractions at 308K. Various acoustical parameters were calculated. The chemicals were used without purification. Specific gravity bottle was used for measuring the density. Multi frequency interferometer (Model M-82S) was used for the ultrasonic velocity measurements. They concluded that between components in the ternary liquid mixture, diethyl ether and isobutyl methyl ketone, molecular interaction and molecular

association form a relationship. They further concluded that frequency for a fixed concentration is inversely proportional to the molecular interaction.

Kumar *et al.* (2014) [163] had investigated on solute-solvent interactions of amino-acids in aqueous solutions of sodium dihydrogen phosphate at different temperatures. The chemicals used were vacuum dried and stored in desiccators over P_2O_5 before use. For the preparations of the solutions triply distilled and degassed water was used. Viscosities were measured by Anton Paar Automated Micro Viscometer (AMV). Densimeter was used to measure the density. Variations were seen in the density and speed of the sound due to the sensitivity of the instrument. They measured the solution densities at temperatures 288.15, 293.15, 298.15, 303.15 and 308.15K.

Saxena (2013) [164] had investigated the acoustics of aqueous polyethylene glycol. Liquid polyethylene glycol was used for investigation. By adding the known volume of polyethylene glycol to fixed volume of water, clear solutions were prepared. Acoustic impedance and ultrasonic absorption were calculated at temperature 35°C at 1MHz frequency using ultrasonic interferometer. By using the thermostatically controlled water bath, the temperature was maintained constant. Pre-calibrated density bottles were used to measure the density. By using standard relations other parameters were calculated. Viscosity and ultrasonic velocity were measured at different temperature and concentrations. It was concluded that the density, acoustic impedance, speed of sound and viscosity rise with the rise in concentration, volume decreases with increase in electrostriction.

Bhidhani *et al.* (2014) [165] had investigated the effect of temperature and concentration on density, viscosity and speed of sound of pentan-1-ol + nitrobenzene mixtures. The chemicals used were purified. Oswald's-Sprengel pycnometer were used to measure the density. Ultrasonic interferometer was used to measure the ultrasonic velocity. The chemicals were experimented out in a thermostatically controlled constant temperature water bath. They concluded that the breaking up of the hydrogen bonds of alcohol and then the formation of hydrogen bond between the unlike component are the reasons for volumetric behavior and viscosity deviation.

Kondaiah *et al.* (2014) [166] calculated the density and viscosity of binary mixtures of EG with amides at the temperature range of 308.15 K. V^E , deviation in viscosity and excess Gibbs free energy of activation of viscous flow is determined from the experimental data. Due to the addition of amide molecules the observed values of deviation/excess properties are found to be negative.

Deosarkar and Ghatbande (2014) [167] studied molecular interactions and structural fittings in binary EG + ethanol and EG + H₂O mixtures by determining the densities, viscosities and molar interactions of both the binary systems. From these properties V^E and excess viscosities were calculated. The strong dipole-dipole interactions between the unlike solvents in both the mixtures rise with rise in mole interactions of EG for both binary systems.

Raman *et al.* (2014) [168] studied the density, viscosity and speed of sound measurements in aqueous DEG solutions at different temperatures. The solute-solvent interactions in aqueous DEG can be understood using the data values obtained from speed of sound and other acoustical parameters. Through this study it was found that the hydration number is 5 which gives us the better understanding for further studies on the structure and intermolecular interaction.

Moattar and Dehghanian (2014) [169] measured the values of density and viscosity for (methoxybenzene + PEG-400) and (ethoxybenzene + PEG-400) at temperature range of (298.15, 308.15 and 318.15) K. From these observed values, the values of excess molar volume and excess Gibbs free energy activation have been determined which are then used in Redlich-Kister type polynomial equation to derive coefficients and standard deviation.

Klimaszewski *et al.* (2015) [170] calculated the sound velocity and density in binary liquid mixture of water and tri-ethylene glycol (TEG) over wide range of temperatures. The values of density were measured at temperature range of (278.15 to 333.15) K whereas for ultrasonic velocity the temperature range was (288.15 to 318.15) K. From

the experimental values, the values of molar volume were calculated which were then used to determine the V_{ϕ}^0 of the mixture components.

Kaur *et al.* (2016) [171] had attempted to investigate and study theoretically the ultrasonic velocity in binary mixture of chloroform and methanol. The ultrasonic velocity measurement was carried out at 295K by using ultrasonic interferometer working at 2MHz. Using Nomoto's relation, Rao's specific velocity relation, Van Dael-Vangeel Ideal mixture relation and Junjie's relation the ultrasonic velocities were computed and compared for the binary mixture of chloroform and methanol. They concluded that the best equation for calculating the ultrasonic velocity is the Junjie's relation. They concluded that the deviation in the obtained parameters shows the presence of the molecular interaction between the molecules of the mixture.

Vigneswaril *et al.* (2016) [172] had examined the molecular interactions of solutions of polyvinyl alcohol. Ultrasonic velocity measurements were carried out by ultrasonic interferometer working at 1MHz. Specific gravity bottle was used to carry out the density measurements. They showed the presence of the molecular interaction from all the calculated acoustical and thermodynamic parameters. They also concluded that the molecular interactions were stronger in case of the binary liquid mixtures than in ternary liquid mixtures. They also identified the mechanism in forming the in ternary mixtures. The competitive mechanism in establishing hydrogen bonding between solute-solvent.

Saini *et al.* (2016) [173] determined the densities, viscosities and speed of sound for the binary mixtures of p-anisaldehyde and various alkanols at the temperature of 303.15 K. From these experimental values various excess parameters are calculated which are then correlated by Redlich-Kister polynomial equation. It was observed that the magnitude and sign of excess parameters play an important role in determining the types of interactions in the binary liquid mixtures.

Sharma *et al.* (2016) [174] studied the viscosities of glycine, L-alanine and L-valine in aqueous tetraethylammonium iodide (TEAI) solutions. With the increase in alkyl chain length of amino acids the viscosities also increase which was discussed in terms of

hydrophobic-hydrophobic interactions. The values of free energy of activation per mole was found to be increasing from glycine to L-valine which indicated that the number of carbon atoms of the side chain increases from glycine to L-valine.

Kumar *et al.* (2016) [175] reported the densities and speeds of sound of mixtures of sodium dodecyl sulphate with alkoxy alkanols. In this study the values observed for apparent volumes were positive which shows dominance of intermolecular hydrophilic interaction between alkoxy alkanols and surfactant molecules whereas for K_ϕ there was no major change in the values with increase in temperature but the values changed with increase in concentration of sodium dodecyl sulphate.

Alisha *et al.* (2017) [176] had determined the ultrasonic studies of benzene with carbitols at different mole fractions at 308.15 K. Different acoustical parameters k_s and Z . Ultrasonic interferometer at a frequency of 2MHz was used to measure the ultrasonic velocity. Pycnometer was used to measure the densities. Due to the molecular interaction among the components of the binary mixtures, different trends in the variation of the parameters are derived.

Godhani *et al.* (2017) [177] had studied the thermodynamic properties of 1,3,4-oxadiazole in chloroform and N, N-dimethyl formamide at three different temperatures 303 K, 308 K and 313 K. Aluminium coated TLC plates were used to check the purity of the chemicals. Ultrasonic interferometer was used for the velocity measurements. Pycnometer was used for the density determination. For determining viscosity Ubbelohde viscometer was used. Their experimental research deduced that density, viscosity and velocity decreases with temperature and increased with concentration. They also concluded that the structure forming was due to the strong molecular interaction due to the positive values of the salvation number. Their study on various thermodynamic parameters on binary mixtures also concluded the presence of the strong and weak dispersive forces.

3.1 OBJECTIVES

Brief objectives of the research are:

- To find ultrasonic velocity, density and viscosity in liquid mixtures of glycols at various compositions and different temperatures.
- To study molecular interactions by calculating various acoustical parameters in liquid mixtures containing glycols at different temperatures.
- To study excess thermodynamic and acoustic properties of liquid mixtures containing glycols.
- To study the comparison between calculated and experimental acoustical data using various theoretical models.

3.2 EXPERIMENTAL PROCEDURES

The experimental work carried out during the present investigations consists of measurements of density ρ , ultrasonic speed c , and viscosity η for binary mixtures of ethylene glycols with glycerol, ternary mixtures of ethylene glycols, polyethylene glycols in aqueous glycerol and aqueous sorbitol solutions at different temperatures and concentrations.

Section I

Ethylene Glycol

Diethylene Glycol + Glycerol + Water

Triethylene Glycol

Section II

Polyethylene Glycol 400

Polyethylene Glycol 4000 + Glycerol + Water

Section III

Ethylene Glycol

Diethylene Glycol

Triethylene Glycol

+ Sorbitol + Water

Section IV

Polyethylene Glycol 400

Polyethylene Glycol 4000

+ Sorbitol + Water

Section V

Ethylene Glycol

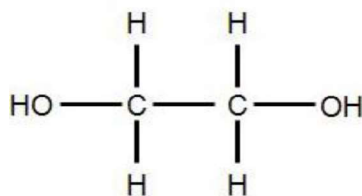
Diethylene Glycol

Triethylene Glycol

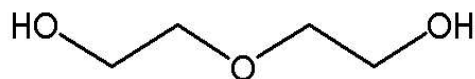
+ Glycerol

3.3 CHEMICAL STRUCTURES OF COMPOUNDS USED FOR STUDY

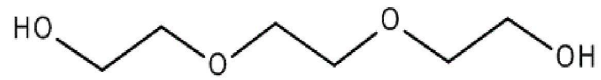
Ethylene Glycol



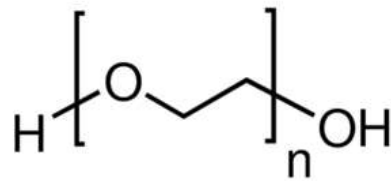
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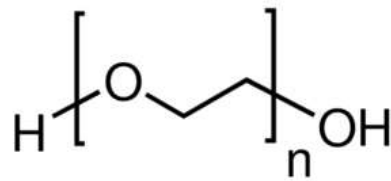
Triethylene Glycol



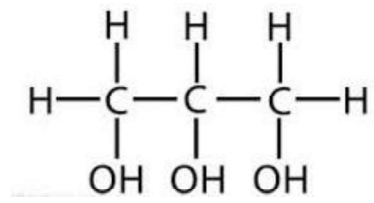
Polyethylene Glycol 400



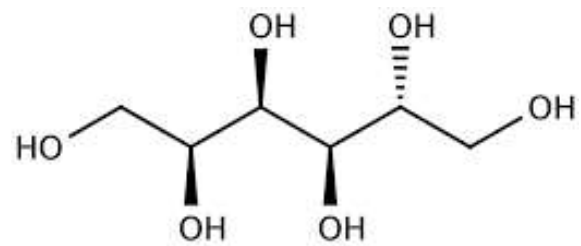
Polyethylene Glycol 4000



Glycerol



Sorbitol



3.4 SPECIFICATIONS OF THE CHEMICALS USED

The specifications of the chemicals used throughout the work are enlisted in following table.

Table 3.1 List of chemicals used and their specifications.

Sr. No.	Chemical	Source	Purification method	Mass fraction purity(supplier)
1.	Ethylene Glycol	Loba Chemie Pvt. Ltd, India	Vacuum drying	≥ 0.99
2.	Diethylene Glycol	SD Fine Chem. Ltd.	Vacuum drying	≥ 0.985
3.	Triethylene Glycol	Loba Chemie Pvt. Ltd, India	Vacuum drying	≥ 0.99
4.	Polyethylene Glycol 400	Loba Chemie Pvt. Ltd, India	Vacuum drying	≥ 0.99
5.	Polyethylene Glycol 4000	Loba Chemie Pvt. Ltd, India	Vacuum drying	≥ 0.99
6.	Glycerol	Loba Chemie Pvt. Ltd, India	Vacuum drying	≥ 0.99
7.	Sorbitol	Loba Chemie Pvt. Ltd, India	Vacuum drying	≥ 0.99

3.5 METHODS AND PREPARATIONS

All chemicals described in **Table 3.1** are attained in their highest purity. The freshly prepared triple distilled and degassed water having specific conductance $<10^{-6} \text{ S}\cdot\text{cm}^{-1}$ has been employed to prepare all the solutions utilized in the measurements. All the liquid samples were equipped by balancing on a Sartorius CPA 225D balance with an accuracy of $\pm 0.00001\text{g}$. To avoid any aging effects the measurements of freshly prepared samples were made on the same day.

3.6 EXPERIMENTAL TECHNIQUES

The methods availed in the present work are as follows:

3.6.1 Ultrasonic speed measurements: The ultrasonic speeds have been measured by two instruments. For the binary systems, ultrasonic interferometer (Mittal enterprises M-80) was employed and for ternary systems Anton Paar DSA 5000M was utilized.

3.6.2 Density measurements: For measuring densities also two methods have been practiced. For binary systems, specific gravity bottle was utilized and for ternary systems Anton Paar DSA 5000M was used.

3.6.3 Viscosity measurements: To obtain the viscosities of liquid mixtures, an Oswald's viscometer was employed.

The brief working description of these instruments

(i) Ultrasonic Interferometer

Ultrasonic interferometer, a direct and simple device to find ultrasonic speed in liquids and liquid mixtures, shown in Figure 3.1. An accurate determination of wavelength (λ) in the medium is the base for principle utilized in measurement of speed (c). Using a quartz crystal, the ultrasonic waves with known frequency (f) are generated. The formation of standing waves occurs in medium if separation among two plates is a whole multiple of sound wavelength. Thus, acoustic resonance is achieved, which results in generation of electrical signal on generator driving quartz crystal and anode current of generator becomes a maximum.

If distance between the plates is decreased or increased and variation exactly become one half of the wavelength or multiple of it, then anode current becomes maximum. Then, from the understanding of wavelength, the ultrasonic speed (c) can be attained by the succeeding relation:

$$c = \lambda \times f$$

Where, c = velocity of wave, λ = wavelength of wave, f = frequency of particle's vibration.

The Ultrasonic Interferometer comprises of following parts:

- a) A High Frequency Generator
- b) A Measuring Cell



Figure 3.1 Ultrasonic interferometer

a) *A High Frequency Generator* has been intended to produce ultrasonic wave in an experimental liquid filled within the measuring cell by exciting quartz crystal, to its resonant frequency placed at bottom of measuring cell. To observe the change in current, a micrometer is provided and for persistence of sensitivity regulation and an initial adjustment of micrometer, two controls are provided high frequency generator panel.

b) *A Measuring Cell*, especially double walled fabricated cell for the constant maintenance of temperature of experimental liquid at the time of experiment. Raising or lowering of reflector plate in liquid sample in cell can be done through the micrometer which has been placed at the top. It also contains a quartz which is fixed at the bottom.

(ii) Specific gravity bottle

A specific gravity bottle with 10 ml capacity shown in Figure 3.2, has been used in the present study. Before using it, the gravity bottle must be dried and cleaned with distilled water. Firstly, weighing (W_0) of the cleaned and dried specific gravity bottle is done and then the distilled water is filled into it. By the means of a stand, the specific gravity bottle has been suspended in thermostat water bath to achieve temperature of the bath. Then, from the water bath the gravity bottle has been removed and with a cotton it is

dried outside and its weight is determined with the help of digital balance (W_1). It is again then washed, dried and now filled with an experimental liquid. By following the same procedure for various temperatures, the weight (W_2) of the sample is evaluated.



Figure 3.2 Specific Gravity bottle

Thus, density of liquids has been calculated using the formula,

$$\rho_2 = (W_2/W_1) \rho_1$$

Where, W_1 = weight of the distilled water, W_2 = weight of experimental solution, ρ_1 = density of water, ρ_2 = density of experimental solution.

(iii) Anton paar DSA 5000M

Anton Paar DSA 5000M densitometer has been utilized for measurement of densities, ρ and ultrasonic speeds, c of aqueous solutions of sugar alcohols and their mixtures with EGs as additives within the temperature range from $T = (288.15$ to $318.15)$ K and 0.1 MPa pressure.



Figure 3.3 Anton Paar DSA 5000 M

This equipment has density and pulse-echo speed of sound cells fitted inside which determine two physically independent properties, density and speed of sound simultaneously with one sample (Figure 3.3 and 3.4). Both the measuring cells are made up of stainless steel and temperature is controlled using a built-in thermostat. Two integrated Pt 100 platinum thermometers together with Peltier elements provide an extremely precise temperature control of ± 0.001 K. this instrument follows the oscillating U-tube principle. When about 3.5 mL of the bubble free sample is introduced into a U-shaped glass tube that is being excited to vibrate at its characteristic frequency electronically, the characteristic frequency changes depending on the density of sample. Through a precise determination of the characteristic and a mathematical conversion, the density of the sample can be measured. Similarly, when the sample enters into the sound velocity measuring cell that is bordered by an ultrasonic transmitter on the one side and by a receiver on the other side, the transmitter sends sound waves of a known period through the sample. Then the speed of sound can be calculated by determining the period of received sound waves and by considering the distance between the transmitter and the receiver.

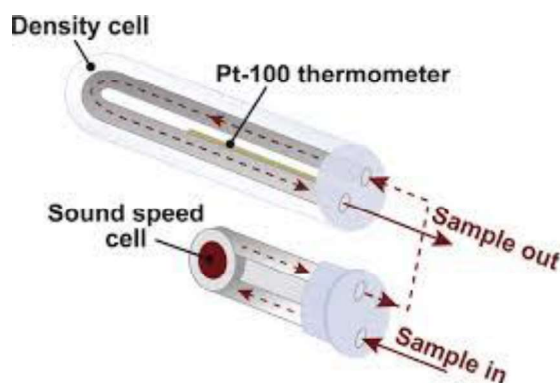


Figure 3.4 Density and sound speed cell of DSA 5000 M

The measuring cells were washed with water and alcohol after every use. The apparatus was first calibrated with double distilled and degassed water and air at different temperatures before each series of measurements. The densities and speed of sound were found to be in good agreements with literature. It can measure densities range from $(0 \text{ to } 3) \text{ g}\cdot\text{cm}^{-3}$ and speed of sound range from $(1000 \text{ to } 2000) \text{ m}\cdot\text{s}^{-1}$.

(iv) Ostwald's viscometer

The Ostwald's viscometer shown in Figure 3.5 is employed for measuring viscosity. Firstly, it is thoroughly cleaned with distilled water and dried. Water about 10 to 25 ml relying on capacity of the bulb is pipetted into it. Then the water is slurped into bulb using a rubber tube linked at end until it rises the mark A. Using stop watch, the time (t_1) taken by water to flow is noted. Viscometer is then dried and by repeating the same process, the same amount of experimental liquid is pipetted into the bulb and the time (t_2) of flow has been noted.

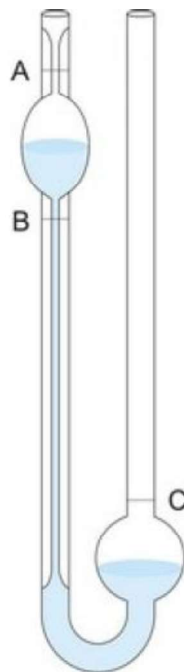


Figure 3.5 Ostwald's viscometer

Then, coefficient of viscosity of liquid mixture is computed from the relation:

$$\eta_2 = \eta_1 (t_2/t_1) (\rho_2/\rho_1)$$

Where, η_1 = viscosity of water, η_2 = viscosity of experimental solution, ρ_1 = density of water, ρ_2 = density of experimental solution, t_1 = time of flow of water, t_2 = time of flow of experimental solution.

3.7 VARIOUS ACOUSTIC PARAMETERS

Various acoustic parameters dependent on velocity, density and viscosity are calculated as follows:

3.7.1 Acoustic impedance (Z)

Acoustic impedance is the resistance offered to the propagation of ultrasonic wave in the medium and can be defined as the product of density (ρ) of the medium and ultrasonic velocity (U) of the same medium. It can be written as

$$Z = \rho \times U$$

3.7.2 Adiabatic compressibility (β)

Adiabatic compressibility is fractional reduction in volume per unit increase of pressure, when no heat flows in or out. This variation is related to the compressibility in a medium by thermodynamic relation:

$$\beta = (1/V) (dV/ dP)$$

Adiabatic compressibility can also be calculated from the ultrasonic velocity (c) and density (ρ) of the medium using equation:

$$\beta = 1/ (c^2 \times \rho)$$

3.7.3 Intermolecular free length (L_f)

In 1952, Jacobson suggested an empirical relation for calculating the intermolecular free length of liquids.^[8] According to the studies, L_f is given by:

$$L_f = K_T \times \beta^{1/2}$$

Where, K_T = Jacobson constant whose value is 2.0965×10^{-6}

β = compressibility of the liquid.

Intermolecular free length can also be expressed in terms of ultrasonic velocity and density as:

$$L_f = K/ (c \times \rho^{1/2})$$

Where, c = ultrasonic velocity of experimental liquid

ρ = density of liquid of experimental liquid.

3.7.4 Ultrasonic Attenuation (α)

Ultrasonic attenuation is a rate of decay of energy when an ultrasonic wave propagates through a medium. The main causes for attenuation in ultrasonic wave are absorption, scattering, reflection, refraction etc. Decrease in the intensity of ultrasonic wave is represented by the ultrasonic wave attenuation coefficient α as:

$$\alpha/f^2 = 8\pi^2\eta / 3\rho c^3$$

Where, f = frequency of the wave.

An ultrasonic attenuation increases with increase in frequency as it is directly proportional to the square of frequency (f) of wave.

3.7.5 Relaxation Time (τ)

The measure of time taken by the particles of a medium to come back to their mean positions within the medium is called relaxation time. Therefore, as long is the relaxation time, more is the absorption of ultrasound energy. Relaxation time for binary mixtures can be given as:

$$\tau = 4\beta\eta/3$$

Relaxation time can also be calculated from:

$$\tau = 4\eta/3\rho c^2$$

3.7.6 Free Volume (V_f)

In the liquids, molecules are not closely packed and there is a free space between the molecules to move within the liquid by obeying laws and is defined as free volume.

It can be calculated by using the formula-

$$V_f = [M_{eff} c / K\eta]^{3/2}$$

Where, K = temperature dependent constant whose value is 4.28×10^9 .

c = ultrasonic velocity in the medium

M_{eff} = effective molecular weight

η = viscosity of the mixture.

3.7.7 Wada's Constant (W)

Wada put forward a relation given by

$$W = (\beta)^{-1/7} M_{eff} / \rho$$

Where, W is Wada's constant, independent of temperature

β is called adiabatic compressibility

ρ is density of mixture

3.7.8 Rao's Constant (R)

The relation between speed of sound (c), effective molecular weight (M_{eff}) of the mixture and density (ρ) of the mixture is given by

$$R = c^{1/3} M_{eff} / \rho$$

Where, R is called Rao's Constant, independent of temperature.

3.7.9 Molar Volume (V_m)

Molar volume is the relation between the effective molecular weight and density of the mixture and is given by-

$$V_m = M_{eff} / \rho$$

Where, M_{eff} = effective molecular weight

ρ = density of the mixture.

3.7.10 Vander Waal's Constant (b)

Vander Waal gave a relation which is dependent on time and is given by-

$$b = V_m [1 - (RT/Mc^2) \{ (1 + (Mc^2/3RT))^{1/2} - 1 \}]$$

Where, R = gas constant having value 8.31451

T = temperature

V_m = molar volume

M = effective molecular weight.

3.7.11 Internal Pressure (π_i)

Internal pressure deals with the forces of attraction and repulsion between the molecules in a liquid. It is a measure of cohesive forces which are the basis for any model of a liquid. It is sensitive to change of temperature, concentration and external pressure. [9]

Internal pressure is determined by using ultrasonic velocity in relation with other thermodynamic parameters and is given by-

$$\Pi_i = bRT [(k\eta/c)^{1/2} (\rho^{2/3} / M^{7/6})]$$

Where, b = cubic packing whose value is 2 for liquids.

R = gas constant having value 8.31451

T = temperature at which experiment has been done

k = dimensionless constant independent of temperature whose value is 4.281×10^9

η = viscosity of experimental liquid mixture

U = ultrasonic velocity in the liquid mixture

ρ = density of experimental liquid

M = effective molecular mass.

3.7.12 Available Volume (V_a)

Available volume can be calculated from the following relation-

$$V_a = M / \rho (1 - U / U_\infty)$$

Where, M = effective molecular weight

ρ = density of experimental liquid

U = ultrasonic velocity in experimental liquid mixture

U_∞ = velocity of sound or ultrasonic velocity at infinity, which is equal to 1600 m/sec.

3.7.13 Gibb's Free Energy (ΔG)

It is the energy associated with chemical reaction that can be used to do work. The change in this energy can be calculated as

$$\Delta G = K_B T \ln (K_B T \tau / h)$$

Where, K_B = Boltzmann's constant whose value is 1.38×10^{-23}

T = absolute temperature (295 K)

τ = relaxation time

h = Planck's constant having value 6.634×10^{-34} .

3.7.14 Enthalpy (H)

Enthalpy is the thermodynamic function which includes internal energy of the system and the product of pressure and volume of the system. Basically, it is a measure of total energy of the thermodynamic system and is denoted by ' H '.

Enthalpy of a system can be calculated as-

$$H = V_m \times \pi_i$$

Where, V_m = molar volume of experimental liquid

π_i = internal pressure of the same experimental liquid.

3.8 THEORETICAL MODELS FOR ULTRASONIC SPEED

Various theories use to calculate theoretical values of ultrasonic speed:

3.8.1 Nomoto's relation:

Nomoto established an empirical relation for ultrasonic speed in binary liquid mixtures as:

$$U_{\text{NOM}} = [(X_1 R_1 + X_2 R_2) / (X_1 V_1 + X_2 V_2)]^3$$

Where molar sound velocity, $R_1 = (M_1 / \rho_1) c_1^{1/3}$ and $R_2 = (M_2 / \rho_2) c_2^{1/3}$

X_1 and X_2 are the mole fractions of 1st and 2nd components of the liquid mixture

Molar volume, $V_1 = (M_1 / \rho_1)$ and $V_2 = (M_2 / \rho_2)$

3.8.2 Impedance dependent relation:

$$U_{\text{IMP}} = (X_1 Z_1 + X_2 Z_2) / X_1 \rho_1 + X_2 \rho_2$$

Where X_i is the mole fraction,

ρ_1 and ρ_2 the density of 1st and 2nd component

Z_1 and Z_2 is the acoustic impedance of 1st and 2nd component.

3.8.3 Van Dael and Vangeel Ideal mixing relation:

$$U_{\text{VDV}} = [(X_1 / M_1 c_1^2 + X_2 / M_2 c_2^2) (X_1 M_1 + X_2 M_2)]^{-1/2}$$

Where M_1 , M_2 are molecular weights of constituent components.

c_1 and c_2 are ultrasonic speeds of individual compounds.

3.8.4 Jungie equation:

$$U_{\text{JUN}} = [(X_1 M_1 / \rho_1 + X_2 M_2 / \rho_2) / (X_1 M_1 + X_2 M_2)^{1/2}] [\{X_1 M_1 / \rho_1 c_1^2 + X_2 M_2 / \rho_2 c_2^2\}]^{-1/2}$$

Where ρ_1 and ρ_2 are the densities of constituent components.

Percentage deviation in ultrasonic speed:

The percentage deviations in ultrasonic velocity between the experimental and theoretical values are calculated as

$$(\Delta c/c) \% = ((c_{\text{EXP}} - c_{\text{THEORY}}) / (c_{\text{EXP}})) \times 100$$

3.9 EXCESS VALUES AND DEVIATIONS OF ACOUSTICAL PARAMETERS

Formulas to calculate some excess values and deviations of acoustical parameters: -

3.9.1 Excess molar volume:

The experimental values of density are used to calculate excess molar volume using following equation: -

$$V^E = (X_1 M_1 + X_2 M_2) / \rho_m - [(X_1 M_1) / \rho_1 + (X_2 M_2) / \rho_2]$$

Where, X_1 = mole fraction of first component

X_2 = mole fraction of second component

3.9.2 Deviation in isentropic compressibility

The deviations in compressibility can be calculated from the following two equations:

$$\Delta \beta = \beta - (X_1 \beta_1 + X_2 \beta_2)$$

β_1 = isentropic compressibility of 1st component

β_2 = isentropic compressibility of 1st component

3.9.3 Viscosity deviations

These can be calculated from mole fractions and experimental values of viscosities of binary mixtures and pure components by using the following equation:

$$\Delta \eta = \eta - (X_1 \eta_1 + X_2 \eta_2)$$

Where, η = viscosity of binary mixture

η_1 = viscosity of first component

η_2 = viscosity of second component

X_1 = mole fraction of first component

X_2 = mole fraction of second component

3.9.4 Excess Gibb's free energy of activation:

It can be calculated from experimental values of molar volumes and viscosities of mixtures and pure components by using the following equation:

$$\Delta G^{*E} = RT [\ln (\eta V) - X_1 \ln (\eta_1 V_1) - X_2 \ln (\eta_2 V_2)]$$

Where, R is universal gas constant and T is absolute temperature.

η = viscosity of binary mixture

V = molar volume of binary mixture

η_1 = viscosity of first component

V_1 = molar volume of first component

η_2 = viscosity of second component

V_2 = molar volume of second component

3.10 APPARENT MOLAR AND PARTIAL MOLAR PROPERTIES

3.10.1 Apparent molar volume

The difference in the volume of the solution and of the pure solvent per mole of solute is defined as the apparent molar volume.

It is the property of the solution which shows the variation in corresponding solution property when that entire component is added to this solution, per mole of component added.

$$V_\phi = M/\rho - (\rho - \rho_0)/m_A \rho \rho_0$$

3.10.2 Partial molar volume

The difference of volume of solution when the mole of solute is added to a huge amount of the solution, where no appreciable change in the total concentration of the solution

at constant temperature, pressure and number of molecules is observed, it is defined as the partial molar volume of a component.

It is the difference in the volume per mole of the substance added to the mixture.

$$V_{\phi} = V_{\phi}^0 + S_V^* m_A$$

3.10.3 Partial molar volume of transfer

The transfer volume of solute from water to the pure solvent system at infinite dilutions was computed with the following formula

$$\Delta V_{\phi}^0 = V_{\phi}^0 \text{ (in pure solvent)} - V_{\phi}^0 \text{ (in water)}$$

3.10.4 Temperature dependent partial molar volume

The change in the apparent molar volume, V_{ϕ}^0 along with temperature at finite dilution is given by the following equation

$$V_{\phi}^0 = a + b(T - T_{ref}) + c(T - T_{ref})^2$$

in which T represents the temperature, $T_{ref} = 298.15$ K, a , b and c represent the empirical constants. These parameters were used to calculate V_{ϕ}^0 and deviations attained from calculated and experimental values. The deviations are calculated from the following equation:

$$\sigma = (1/n) \Sigma [abs((Y_{exptl.} - Y_{calc.})/Y_{exptl.})]$$

Where $Y = V_{\phi}^0$ (apparent molar volume at infinite dilution).

At infinite dilution, the temperature dependence of partial molar volume (V_{ϕ}^0) can be uttered in terms of absolute temperature (T) by the following equation. The same equation is used to calculate partial molar expansibilities as follows:

$$E_{\phi}^0 = (\partial V_{\phi}^0 / \partial T)_p = b + 2c(T - T_{ref})$$

The following thermodynamic expression determined the structure making and breaking ability of solute in solvent using the following equation:

$$(\partial E_{\phi}^0 / \partial T)_p = (\partial^2 V_{\phi}^0 / \partial T^2)_p = 2c$$

3.10.5 Apparent molar isentropic compression

By using the following equation, apparent molar isentropic compression of solute in the aqueous solution of a chemical sample is calculated

$$K_{\phi,s} = (Mk_s/\rho) - \{(k_{s,0}\rho - k_s\rho_0)/m_A\rho\rho_0\}$$

Where m_A , M , ρ , ρ_0 , $k_{s,0}$ and k_s are the molality of solute, the molar mass of the solute, density of the solvent and the solution, isentropic compressibility of the pure solvent and the solution accordingly. The isentropic compressibility is determined by the following expression-

$$k_s = 1/c^2\rho$$

Where ρ and c are the density and ultrasonic velocity of the solution respectively.

3.10.6 Partial molar isentropic compression

By the following equation, the change in apparent molar isentropic compression $K_{\phi,s}$ with the molar concentration is given as

$$K_{\phi,s} = K_{\phi,s}^o + S_K^* m_A$$

Where, S_K^* is an experimental slope suggestive of solute-solute interactions.

3.10.7 Partial molar isentropic compression of transfer

At infinite dilution, the partial molar isentropic compressions $\Delta K_{\phi,s}^o$ of glycols in aqueous solution of chemical sample is calculated with the following equation

$$\Delta K_{\phi,s}^o = K_{\phi,s}^o (\text{in aqueous chemical sample}) - K_{\phi,s}^o (\text{in water})$$

3.10.8 Pair and triplet interaction coefficients

From the following relation, the partial molar volume of transfer and the partial molar isentropic compression of transfer can be obtained:

$$\Delta V_{\phi}^o (\text{water to aqueous chemical sample solution}) = 2V_{AB}m_B + 3V_{ABB}m_B^2$$

$$\Delta K_{\phi,s}^o (\text{water to aqueous chemical sample solution}) = 2K_{AB}m_B + 3K_{ABB}m_B^2$$

Where A represent glycols and B represent chemical sample and m_B denotes the molality of the aqueous chemical sample solutions. The pair and triplet interaction coefficient are represented by the parameters V_{AB} and V_{ABB} for volume, and K_{AB} , K_{ABB} for isentropic compression.

Section I

In this section, we have reported the densities, ρ and speed of sound c of ethylene glycol (EG), diethylene glycol (DEG) and triethylene glycol (TEG) in (0.00, 0.01, 0.03, 0.05) mol·kg⁻¹ aqueous solutions of glycerol at temperatures $T = (293.15, 298.15, 303.15, 308.15)$ K.

Density

The experimental densities, ρ obtained for EG, DEG and TEG in (0.00, 0.01, 0.03, 0.05) mol·kg⁻¹ aqueous solutions of glycerol are enlisted in Table 4.1. It is observed from analysis of Table 4.1, that the values of densities are increasing with increase in concentration of glycols and decreasing with increase in temperature. The measured densities for the mixtures of (EG + water, DEG + water and TEG + water) are compared with literature [39, 45, 46, 88, 98, 122, 130, 145, 161, 168, 170, 178] densities and are represented in Figures 4.1 to 4.3. From Figures 4.1 and 4.3, it is noticed that experimental values of density for (EG + water and TEG + water) follow the same trend as of literature values, but in Figure 4.2 the experimental densities for (DEG + water) are in coherence with all the literature [39, 45, 122, 161 and 178] values except for the values reported in reference [168]. The values of densities for (DEG + water) reported in reference [168] shows deviations from experimental values and also from literature values reported in reference [161 and 178] at temperature 303.15 K and 308.15 K. The comparison for the densities of liquid mixtures (glycerol + water) with the literature [120, 144 and 179] has also been done and is represented in Figure 4.4. The experimental densities are found to be in trend with the literature values given in reference [144 and 179] but a little deviation has been observed from the values reported in reference [120] at temperature 303.15 K and 308.15 K. Further, the observed experimental densities for ethylene glycol in aqueous glycerol solutions have been compared with literature [180] values and are exhibited in Figure 4.5.

Apparent molar volume

The experimental values of densities are used to calculate the values of apparent molar volume (V_ϕ) from the following equation:

$$V_\phi = (M/\rho) - \{(\rho - \rho_0)/(m_A \rho \rho_0)\} \quad (4.1)$$

where M is the molar mass ($\text{kg}\cdot\text{mol}^{-1}$) of the solute, m_A is the molality ($\text{mol}\cdot\text{kg}^{-1}$) of the glycols *i.e.* amount of solute (glycols) per one kilogram of the solvent (mixture of water + glycerol) and ρ_0 and ρ are the densities ($\text{kg}\cdot\text{m}^{-3}$) of the solvent and solution, respectively. The calculated values of apparent molar volume, are given in Table 4.1. All the computed values of apparent molar volume, are positive due to large intrinsic volume of solute which indicate strong solute-solvent interactions in the present ternary system. The values described in Table 4.1 reveals that the values of apparent molar volume surge with upsurge in concentration of glycerol which may be due to the fact that with the increase in concentration of glycerol, water molecules in the first hydration shell become more likely to be associated with the glycerol OH groups than the alkyl backbone [65] which indicate that glycerol molecules interact constructively with water to strengthen H-bond network in the solvent [181]. Further, the apparent molar volumes increase with increase in molar mass of glycols *i.e.* from EG to TEG at all concentrations of glycerol and all temperatures. This increase in V_ϕ values can be attributed to the factors hydrophilic effect, hydrophobic hydration in water-rich region, physical forces such as dipole-dipole and dipole-induced dipole interactions [146].

Partial molar volume

By the means of least squares fitting of apparent molar volume V_ϕ , partial molar volume V_ϕ^0 is calculated from the following equation:

$$V_\phi = V_\phi^0 + S_V^* m_A \quad (4.2)$$

where S_V^* an experimental slope, is the semi-empirical solute-solute interaction coefficient and m_A is the molality of glycols in aqueous glycerol solutions. In Table 4.2 the values of V_ϕ^0 and S_V^* along with standard errors are listed. The standard errors are computed from

V_ϕ values by least squares fitting of it to equation 4.2. All the values of V_ϕ^0 are positive and increase with increase in temperature and concentration of glycerol in all the three glycols as represented in Figure 4.6. This increase in V_ϕ^0 values suggests that contribution of oxyethylene group increases with increase in temperature [161]. The increasing concentration of glycerol strengthens the H-bond network in the solvent due to constructive interaction among the molecules of water and glycerol [181]. The IR spectral studies by Zhang *et al.* [119] shows that hydrogen bonding interactions are possible in H-atoms of water and OH-atoms of glycols by cross-linking in the form of --H-O-H-- bonding. Further, the V_ϕ^0 values increase with increase in molar mass of glycols at each temperature. Since TEG has one additional -CH₂-CH₂-O- group compared to DEG and two additional -CH₂-CH₂-O- groups compared to EG, therefore results in highest V_ϕ^0 values in case of TEG. The reasons for change in partial molar volume can be attributed to the weakening of H-bond, thermal expansion, release of molecules from solvation layer etc. The difference in V_ϕ^0 values from EG to TEG is very large which suggests that interaction between unlike molecules is very much influenced by the size of hydrocarbon chain [91]. It can also be seen from Table 3 that for all the concentrations of glycerol at all temperatures, the magnitude of S_V^* is positive except for TEG in aqueous solution of 0.05 mol·kg⁻¹ glycerol at temperature 293.15 K and 303.15 K. These positive values of S_V^* indicate that the solute-solute interactions are present in the solutions of glycols in glycerol. Since the values of S_V^* are not showing regular trend, which shows that the solute-solute interactions are influenced by some other factors also [182]. The solute-solvent interaction is predominant over solute-solute interaction because of smaller values of S_V^* as compared to larger V_ϕ^0 values.

Partial molar volume of transfer

The transfer volume of glycols from water to aqueous glycerol solutions at infinite dilution was calculated from following equation

$$\Delta V_\phi^0 = V_\phi^0 \text{ (in aqueous glycerol)} - V_\phi^0 \text{ (in water)} \quad (4.3)$$

The computed values of ΔV_{ϕ}^0 are indexed in Table 4.3. All the values of ΔV_{ϕ}^0 are positive and are increasing with increasing concentration of glycerol for each glycol, which infers huge desiccation effect on glycols. No regular trend is found in ΔV_{ϕ}^0 values with respect to increase in temperature. The obtained positive values of ΔV_{ϕ}^0 propose strong molecular interactions of glycerol with glycols. Pauling [183, 184] described the models regarding pure water structure and assumed that lot of space is available in the water structure in form of empty areas known as clathrates which the other molecules can easily penetrate. Probably very small amounts of EGs can be placed in the cages of the water structures so as not to abolish the cage structure. Rather higher content of glycol destroys a cage structure and there is possibility that organic molecules and water undergoes hydrogen bond formation, new structures are created [170]. The structure making ability of the solute in the solution is promoted due to interactions between solute and solvent molecules as the structural moiety of glycerol and glycol contains polar group.

Temperature dependent partial molar volume

By using general polynomial equation, variation of apparent molar volumes with the temperature at infinite dilution can be expressed as follows

$$V_{\phi}^0 = a + b(T - T_{ref}) + c(T - T_{ref})^2 \quad (4.4)$$

where a , b , c are empirical constants, $T_{ref} = 298.15\text{K}$ and T is the temperature in Kelvin. In aqueous glycerol, the value of these constants for EG, DEG and TEG are indexed in Table 4.4. These parameters were used to calculate V_{ϕ}^0 and deviations attained from calculated and experimental values are also indexed in Table 4.4. The deviations are calculated from the following equation:

$$\sigma = (1/n) \Sigma[\text{abs}((Y_{exptl.} - Y_{calc.})/Y_{exptl.})] \quad (4.5)$$

where $Y = V_{\phi}^0$ (apparent molar volume at infinite dilution). The values listed in Table 4.4 for deviations are very small which fits into the polynomial equation very finely which is evident from R^2 values in the present study.

At infinite dilution, the temperature dependence of partial molar volume (V_{ϕ}^0) can be uttered in terms of absolute temperature (T) by the following equation (4.6). The same equation (4.6) is used to calculate partial molar expansibilities as follows:

$$E_{\phi}^0 = (\partial V_{\phi}^0 / \partial T)_p = b + 2c(T - T_{ref}) \quad (4.6)$$

The limiting apparent molar expansibility at infinite dilution, $E_{\phi}^0 = (\partial V_{\phi}^0 / \partial T)_p$ is considered to be a beneficial measure [185] of solute-solvent interaction existing in the solution. The general thermodynamic expression, developed by Hepler [186] determined the structure making and breaking ability of solute in solvent using the following equation:

$$(\partial E_{\phi}^0 / \partial T)_p = (\partial^2 V_{\phi}^0 / \partial T^2)_p = 2c \quad (4.7)$$

The structure making and breaking ability of solute in solvent can be determined [66, 67] by the sign of $(\partial E_{\phi}^0 / \partial T)_p$. The positive and very small negative values of $(\partial E_{\phi}^0 / \partial T)_p$ observed for structure making solutes whereas negative values of $(\partial E_{\phi}^0 / \partial T)_p$ observed for solutes having structure breaking capacity. The value of partial molar expansibilities E_{ϕ}^0 and $(\partial E_{\phi}^0 / \partial T)_p$ are attributed in Table 4.5. The values of limiting apparent molar expansibility, are positive at all temperatures and concentrations of glycerol. The positive E_{ϕ}^0 values indicate that the solute-solvent interactions are present in these systems, as already suggested by apparent molar volume data. The values of E_{ϕ}^0 show an irregular trend with an increase in the temperature as well as in the concentration of glycerol solutions. The positive and small negative $(\partial E_{\phi}^0 / \partial T)_p$ values for the mixtures of glycols suggests the structure making capability of glycols in all aqueous glycerol solutions.

Ultrasonic speed

The experimental values of ultrasonic speed, c of EG, DEG and TEG in (0.00, 0.01, 0.03, 0.05) mol·kg⁻¹ aqueous solutions of glycerol are measured at temperatures $T = (293.15, 298.15, 303.15, 308.15)$ K. The values of ultrasonic speed of all the mixed solutions at

different temperatures are given in Table 4.6. The experimental ultrasonic speeds for (EG + water, DEG + water and TEG + water) have been compared with the literature values [39, 88, 159, 168, 170, 178] and are represented graphically in Figures 4.7 to 4.9. The experimental ultrasonic speeds for (glycerol + water) have also been compared with literature values [120 and 144] and are represented in Figure 4.10. From the Figures 4.7 to 4.9, it has been scrutinized that experimental and literature values exhibit same trend except for values reported in reference [168]. The ultrasonic speeds reported in reference [168] shows deviation from experimental values as well as from literature values reported in reference [178] at temperature 303.15 K and 308.15 K. As seen from Figure 4.10, experimental ultrasonic speeds for (glycerol + water) are in sequence with the literature values referred in [144] but shows deviations from the literature values described in reference [120]. It is observed from the Table 4.6 that the values of ultrasonic speed vary in sequence with respect to temperature. This increase in ultrasonic speed values relating to temperature is characteristic for water and is concerned with the 3-dimensional network of hydrogen bonds in the structure of water [170]. The increase in ultrasonic speed in any solution indicates the larger association amongst the molecules of the solution. The larger association is because of intramolecular hydrogen bonding between solute molecules itself and intermolecular hydrogen bonds among solute and solvent molecule [168]. It has also been noticed that the ultrasonic speed increases with increase in concentration of glycerol as the glycerol molecules interact constructively with water to support H-bond network in the solvent [145]. The DFT and ultrasonic studies on intermolecular association in hydrogen bonding in aqueous solutions of glycerol have also confirmed the formation of hydrogen bonds between water and hydrophilic hydroxyl groups in a particular hydrated pattern of solutes [120]. Further, the values of ultrasonic speed increase with increase in molality of glycols for a particular concentration of glycerol. Probably, during the addition of glycol to the solvent, hydrogen bonds between glycerol and water molecules get weakened and are destroyed. At the same time, new hydrogen bonds between molecules of solvent and molecules of glycols are formed [170].

Apparent molar isentropic compression

The following equation was used to determine the apparent molar isentropic compression for glycols in aqueous and mixed aqueous solutions of glycerol at different temperatures

$$K_{\phi,s} = (Mk_s/\rho) - \{(k_{s,o}\rho - k_s\rho_o)/m_A\rho\rho_o\} \quad (4.8)$$

where M is the molar mass of the solute ($\text{kg}\cdot\text{mol}^{-1}$), ρ and ρ_o are the densities ($\text{kg}\cdot\text{m}^{-3}$) of the solution and solvent, respectively; m_A is the molality ($\text{mol}\cdot\text{kg}^{-1}$) of glycols i.e. amount of solute (glycol) per one kilogram of solvent (mixture of water + glycerol), k_s and $k_{s,o}$ are the isentropic compressibility's of solution and pure solvent, respectively. The following relation is used to calculate isentropic compressibility

$$k_s = 1/c^2\rho \quad (4.9)$$

where c is ultrasonic speed and ρ is density of solution. The computed values of $K_{\phi,s}$ for various molar concentrations, m_A of EG, DEG and TEG in (0.00, 0.01, 0.03 and 0.05) $\text{mol}\cdot\text{kg}^{-1}$ glycerol at different temperatures are listed in Table 4.6. From the calculated values, it is analyzed that the $K_{\phi,s}$ values are negative at all concentrations of glycerol and at all temperatures. These values of $K_{\phi,s}$ become less negative with increase in temperature because of expansion of the system at higher temperatures. In the liquid mixtures, the most favored and polar EG molecules form more compact structure with solvent molecules through inter-molecular hydrogen bonding resulting in compressibility of the solution which further suggests the strong solute-solvent interactions between the molecules of glycols and the molecules of glycerol [168]. The negative $K_{\phi,s}$ values indicate that the water molecules around solute are less compressible than the water molecules in the solution [188, 189] resulting in the tightening of the water molecules around it because of hydrophobic interactions of a non-polar group. Therefore, the pressure on water molecules in the solution results in compressibility of the solution, which further suggests the strong solute-solvent interactions between the molecules of glycols and the molecules of glycerol.

Partial molar isentropic compression

The partial molar isentropic compression ($K_{\phi,s}^o$) can be calculated by observing the variation of apparent molar isentropic compression ($K_{\phi,s}$) with molal concentration and is represented the following equation:

$$K_{\phi,s} = K_{\phi,s}^o + S_K^* m_A \quad (4.10)$$

Where S_K^* is an experimental slope suggestive of solute-solute interactions and m_A is the molality of glycols in aqueous glycerol solutions. The $K_{\phi,s}^o$ values and S_K^* values together with standard errors derived by the method of least squares fitting are indexed in Table 4.7 and are represented in Figure 4.11. As observed from Table 4.7, the solute-solute interactions are negligible at infinite dilution since the S_K^* values are small in size which further suggests that solute-solvent interactions [190] are dominant in the mixtures. The values of $K_{\phi,s}^o$ are found to be negative such that with the increase in temperature and concentration of glycerol, these values become less negative. The larger negative values of $K_{\phi,s}^o$ for glycols at low temperature suggest strong attractive interactions among the molecules of glycols and water [191]. Further the attractive interaction between glycerol and water molecules induces dehydration of glycol, due to which at higher concentrations of glycerol, the water molecules around the glycols are more compressible than those at lower glycerol concentrations.

Partial molar isentropic compression of transfer

For each glycol from water to aqueous glycerol solutions, the partial molar isentropic compressions of transfer ($\Delta K_{\phi,s}^o$) at infinite dilution were calculated using following equation:

$$\Delta K_{\phi,s}^o = K_{\phi,s}^o (\text{in aqueous glycerol}) - K_{\phi,s}^o (\text{in water}) \quad (4.11)$$

The values of $\Delta K_{\phi,s}^o$ are reported in Table 4.8. All the values of $\Delta K_{\phi,s}^o$ are found to be positive at all temperatures and all concentrations of glycerol except for DEG in 0.05 mol·kg⁻¹ aqueous solution of glycerol at 293.15 K. From the table, it is deduced that with an increase in concentration of glycerol, $\Delta K_{\phi,s}^o$ values also increase except for DEG in 0.05

mol·kg⁻¹ aqueous solutions of glycerol at 293.15 K. The positive values of $\Delta K_{\phi,s}^o$ infer the structure making tendency of solute and dominance of interactions between glycols and glycerol. With increasing concentration of glycerol, the interaction between glycols and glycerol intensifies. With the rise in concentration of glycerol, the structure making capability of the solute increases. As a result, in comparison to the pure solvent, the solution is more compressible which further leads to much fall in compressibility with rising glycerol concentration [192-194]. Therefore, $\Delta K_{\phi,s}^o$ values are positive and $K_{\phi,s}^o$ values are negative for all three glycols with different concentrations of glycerol.

Pair and triplet interaction coefficients

McMillan and Mayer [195] formulated the theory to study the separation of effects due to the pair and triplet interactions. The interaction coefficients are calculated based upon McMillan-Mayer [195]. This theory was further discussed by Friedman and Krishnan [196] and Franks *et al.* [197] so that solute-cosolute interactions can be included in the solvation spheres. So, limiting apparent molar volume of transfer and limiting apparent molar isentropic compression of transfer can be expressed as:

$$\Delta V_{\phi}^o(\text{water to aqueous glycerol solution}) = 2V_{AB}m_B + 3V_{ABB}m_B^2 \quad (4.12)$$

$$\Delta K_{\phi,s}^o(\text{water to aqueous glycerol solution}) = 2K_{AB}m_B + 3K_{ABB}m_B^2 \quad (4.13)$$

where A denotes the glycol, B denotes glycerol and m_B is the molality of aqueous glycerol solutions. The pair and triplet coefficients are denoted by the corresponding parameters V_{AB}, V_{ABB} for volume and K_{AB}, K_{ABB} for isentropic compression. The ΔV_{ϕ}^o and $\Delta K_{\phi,s}^o$ values are fitted to the above equations to calculate the values of constants (V_{AB}, V_{ABB}, K_{AB} and K_{ABB}) and are stated in Table 4.9. For all glycols, the pair interaction coefficients V_{AB} is positive and triplet interaction coefficient V_{ABB} is also positive at all temperatures except for DEG at 293.15 and 303.15 K. The pair interaction coefficient K_{AB} is positive for all glycols at all temperatures. The triplet interaction coefficient K_{ABB} is negative for all glycols except for EG and TEG at temperature 303.15 K. The positive values of pair interaction coefficients for volumetric and compressibility measurements (V_{AB} and K_{AB}) predict [198, 199] that pair wise interactions are dominating in glycol-glycerol-water mixtures.

Table 4.1

Values of densities, ρ , and apparent molar volumes, V_ϕ of glycols in aqueous solutions of glycerol at different temperatures and experimental pressure, $p = 0.1$ MPa.

$^a m_A$ (mol·kg ⁻¹)	$\rho \times 10^{-3}$ (kg·m ⁻³)					$V_\phi \times 10^6$ (m ³ ·mol ⁻¹)						
	$T=293.15$ K	$T=298.15$ K	$T=303.15$ K	$T=308.15$ K	$T=293.15$ K	$T=298.15$ K	$T=303.15$ K	$T=308.15$ K	$T=293.15$ K	$T=298.15$ K	$T=303.15$ K	$T=308.15$ K
<i>EG + 0.00 mol·kg⁻¹ Glycerol</i>												
0.00000	0.99821	0.99705	0.99566	0.99404								
0.09889	0.99906	0.99788	0.99647	0.99484	53.53	53.77	53.98	54.20				
0.19894	0.99988	0.99869	0.99726	0.99561	53.65	53.87	54.11	54.35				
0.29967	1.00068	0.99947	0.99803	0.99636	53.77	53.98	54.21	54.47				
0.39481	1.00141	1.00018	0.99873	0.99704	53.89	54.09	54.31	54.59				
0.50155	1.00220	1.00096	0.99948	0.99776	53.99	54.19	54.44	54.72				
<i>EG + 0.01 mol·kg⁻¹ Glycerol</i>												
0.00000	0.99845	0.99731	0.99587	0.99425								
0.10554	0.99935	0.99819	0.99673	0.99510	53.61	53.82	54.05	54.25				
0.19950	1.00011	0.99894	0.99747	0.99582	53.72	53.94	54.16	54.39				
0.30122	1.00092	0.99972	0.99823	0.99657	53.83	54.06	54.28	54.52				
0.38815	1.00157	1.00037	0.99887	0.99718	53.95	54.15	54.38	54.63				
0.49426	1.00234	1.00113	0.99961	0.99790	54.06	54.26	54.50	54.77				
<i>EG + 0.03 mol·kg⁻¹ Glycerol</i>												

0.00000	0.99887	0.99771	0.99630	0.99468				
0.09813	0.99968	0.99849	0.99707	0.99544	53.82	54.11	54.35	54.62
0.19827	1.00046	0.99926	0.99783	0.99617	53.97	54.26	54.47	54.74
0.30069	1.00124	1.00002	0.99857	0.99689	54.09	54.37	54.59	54.87
0.39774	1.00195	1.00070	0.99925	0.99755	54.19	54.48	54.68	54.96
0.49630	1.00266	1.00139	0.99993	0.99821	54.27	54.56	54.75	55.03
<i>EG + 0.05 mol·kg⁻¹ Glycerol</i>								
0.00000	0.99929	0.99812	0.99672	0.99509				
0.09871	1.00007	0.99888	0.99747	0.99583	54.17	54.41	54.63	54.85
0.20179	1.00086	0.99966	0.99823	0.99657	54.26	54.48	54.68	54.91
0.30048	1.00159	1.00038	0.99894	0.99726	54.32	54.54	54.73	54.98
0.40056	1.00232	1.00109	0.99963	0.99794	54.37	54.60	54.79	55.04
0.49986	1.00303	1.00178	1.00031	0.99859	54.42	54.64	54.85	55.11
<i>DEG + 0.00 mol·kg⁻¹ Glycerol</i>								
0.00000	0.99821	0.99705	0.99566	0.99404				
0.09849	0.99965	0.99846	0.99707	0.99544	91.55	91.89	91.96	92.23
0.19736	1.00103	0.99978	0.99839	0.99678	91.85	92.25	92.33	92.46
0.29505	1.00236	1.00103	0.99964	0.99805	92.11	92.50	92.58	92.64
0.41013	1.00386	1.00249	1.00105	0.99947	92.24	92.58	92.81	92.85
0.50063	1.00499	1.00359	1.00215	1.00053	92.43	92.69	92.90	93.02
<i>DEG + 0.01 mol·kg⁻¹ Glycerol</i>								

0.00000	0.99845	0.99731	0.99587	0.99425					
0.09949	0.99988	0.99868	0.99728	0.99563	91.77	92.06	92.16	92.65	
0.19890	1.00126	1.00002	0.99863	0.99698	91.93	92.24	92.32	92.62	
0.31059	1.00277	1.00148	1.00004	0.99840	92.08	92.38	92.63	92.83	
0.38936	1.00380	1.00246	1.00100	0.99939	92.20	92.51	92.79	92.91	
0.50142	1.00522	1.00383	1.00235	1.00069	92.31	92.65	92.93	93.14	
<i>DEG + 0.03 mol·kg⁻¹ Glycerol</i>									
0.00000	0.99887	0.99771	0.99630	0.99468					
0.10019	1.00027	0.99908	0.99767	0.99603	92.14	92.42	92.68	92.99	
0.19894	1.00162	1.00039	0.99895	0.99731	92.29	92.55	92.85	93.11	
0.28890	1.00280	1.00155	1.00008	0.99844	92.27	92.66	92.98	93.21	
0.39933	1.00421	1.00290	1.00142	0.99977	92.22	92.81	93.13	93.34	
0.50046	1.00546	1.00408	1.00265	1.00097	92.35	92.97	93.24	93.45	
<i>DEG + 0.05 mol·kg⁻¹ Glycerol</i>									
0.00000	0.99929	0.99812	0.99672	0.99509					
0.09939	1.00066	0.99945	0.99803	0.99639	92.29	92.81	93.13	93.39	
0.19981	1.00199	1.00078	0.99932	0.99768	92.41	92.71	93.11	93.32	
0.29813	1.00329	1.00202	1.00054	0.99888	92.39	92.85	93.21	93.46	
0.40035	1.00461	1.00329	1.00177	1.00012	92.40	92.88	93.30	93.51	
0.50015	1.00587	1.00447	1.00296	1.00129	92.41	92.99	93.33	93.54	
<i>TEG + 0.00 mol·kg⁻¹ Glycerol</i>									

0.00000	0.99821	0.99705	0.99566	0.99404					
0.09650	1.00031	0.99913	0.99773	0.99610	128.37	128.69	128.91	129.25	
0.20020	1.00246	1.00127	0.99986	0.99822	128.59	128.85	129.12	129.42	
0.29205	1.00429	1.00311	1.00167	1.00001	128.77	128.97	129.29	129.60	
0.39856	1.00636	1.00514	1.00369	1.00203	128.89	129.15	129.45	129.76	
0.49879	1.00822	1.00699	1.00554	1.00385	129.01	129.28	129.56	129.89	
<i>TEG + 0.01 mol·kg⁻¹ Glycerol</i>									
0.00000	0.99845	0.99731	0.99587	0.99425					
0.09918	1.00059	0.99943	0.99798	0.99635	128.49	128.81	129.09	129.40	
0.20037	1.00269	1.00151	1.00005	0.99841	128.64	128.95	129.23	129.53	
0.30083	1.00469	1.00349	1.00202	1.00036	128.82	129.13	129.39	129.72	
0.40057	1.00660	1.00536	1.00391	1.00222	128.95	129.32	129.51	129.88	
0.49903	1.00843	1.00716	1.00571	1.00399	129.07	129.46	129.64	130.03	
<i>TEG + 0.03 mol·kg⁻¹ Glycerol</i>									
0.00000	0.99887	0.99771	0.99630	0.99468					
0.09994	1.00098	0.99981	0.99839	0.99676	128.85	129.09	129.42	129.69	
0.20031	1.00302	1.00184	1.00040	0.99877	129.03	129.25	129.59	129.83	
0.29980	1.00497	1.00377	1.00238	1.00073	129.16	129.43	129.54	129.82	
0.39952	1.00687	1.00563	1.00425	1.00258	129.23	129.58	129.67	129.98	
0.50056	1.00880	1.00749	1.00614	1.00442	129.17	129.62	129.67	130.05	
<i>TEG + 0.05 mol·kg⁻¹ Glycerol</i>									

0.00000	0.99929	0.99812	0.99672	0.99509				
0.10034	1.00137	1.00019	0.99878	0.99714	129.23	129.51	129.79	130.04
0.20070	1.00339	1.00223	1.00077	0.99916	129.31	129.38	129.83	129.91
0.29991	1.00537	1.00415	1.00272	1.00111	129.21	129.51	129.74	129.88
0.39955	1.00730	1.00600	1.00462	1.00295	129.19	129.67	129.74	130.03
0.50015	1.00918	1.00782	1.00645	1.00479	129.21	129.74	129.82	130.07

^a m_A is the molality of glycols in aqueous glycerol solutions; Standard uncertainties u are $u_r(m) = 1\%$, $u(T) = 0.001$ K, $u(\rho) = 0.05$ kg·m⁻³ and $u(p) = 0.01$ MPa.

Table 4.2

Limiting apparent molar volumes, V_{ϕ}^0 , and experimental slopes, S_V^* of glycols in aqueous solutions of glycerol at different temperatures.

${}^a m_B$	$S_V^* \times 10^6 \text{ (m}^3 \cdot \text{kg} \cdot \text{mol}^{-2}\text{)}$							
	$T=293.15 \text{ K}$	$T=298.15 \text{ K}$	$T=303.15 \text{ K}$	$T=308.15 \text{ K}$	$T=293.15 \text{ K}$	$T=298.15 \text{ K}$	$T=303.15 \text{ K}$	$T=308.15 \text{ K}$
$V_{\phi}^0 \times 10^6 \text{ (m}^3 \cdot \text{mol}^{-1}\text{)}$								
EG								
0.00	53.42(± 0.01)	53.49(± 0.02)	53.73(± 0.01)	54.12(± 0.01)	1.16(± 0.03)	1.17(± 0.02)	1.13(± 0.03)	0.61(± 0.03)
0.01	53.66(± 0.02)	53.71(± 0.01)	54.02(± 0.01)	54.36(± 0.02)	1.06(± 0.03)	1.13(± 0.03)	1.13(± 0.01)	0.58(± 0.02)
0.03	53.88(± 0.03)	53.93(± 0.03)	54.27(± 0.03)	54.57(± 0.01)	1.12(± 0.08)	1.16(± 0.07)	1.02(± 0.02)	0.55(± 0.07)
0.05	54.08(± 0.02)	54.12(± 0.01)	54.53(± 0.01)	54.78(± 0.02)	1.28(± 0.05)	1.32(± 0.03)	1.05(± 0.02)	0.65(± 0.01)
DEG								
0.00	91.52(± 0.16)	91.81(± 0.12)	91.82(± 0.09)	92.06(± 0.02)	1.87(± 0.47)	1.89(± 0.35)	2.32(± 0.28)	1.94(± 0.05)
0.01	91.69(± 0.09)	91.93(± 0.02)	91.96(± 0.05)	92.45(± 0.08)	1.06(± 0.26)	1.46(± 0.06)	2.02(± 0.16)	1.28(± 0.24)
0.03	92.15(± 0.07)	92.28(± 0.01)	92.60(± 0.06)	92.89(± 0.02)	0.34(± 0.21)	1.36(± 0.04)	1.20(± 0.19)	1.07(± 0.05)
0.05	92.31(± 0.04)	92.69(± 0.07)	93.04(± 0.04)	93.29(± 0.06)	0.23(± 0.13)	0.53(± 0.22)	0.60(± 0.12)	0.49(± 0.17)
TEG								
0.00	128.26(± 0.05)	128.55(± 0.01)	128.78(± 0.04)	129.10(± 0.02)	1.57(± 0.14)	1.48(± 0.03)	1.62(± 0.11)	1.61(± 0.07)
0.01	128.35(± 0.02)	128.63(± 0.02)	128.96(± 0.01)	129.23(± 0.02)	1.47(± 0.06)	1.67(± 0.05)	1.38(± 0.04)	1.61(± 0.05)
0.03	128.84(± 0.09)	128.98(± 0.05)	129.41(± 0.06)	129.61(± 0.05)	0.84(± 0.27)	1.38(± 0.16)	0.57(± 0.18)	0.89(± 0.14)
0.05	129.28(± 0.05)	129.34(± 0.09)	129.80(± 0.05)	129.93(± 0.10)	-0.16(± 0.15)	0.74(± 0.29)	-0.04(± 0.15)	0.18(± 0.30)

^a m_B is the molality of aqueous solutions of glycerol.

Table 4.3

Partial molar volume of transfer, ΔV_{ϕ}^o of glycols in aqueous solutions of glycerol at different temperatures.

${}^a m_B$ (mol·kg ⁻¹)	$\Delta V_{\phi}^o \times 10^6$ (m ³ ·mol ⁻¹)			
	$T= 293.15$ K	$T= 298.15$ K	$T= 303.15$ K	$T= 308.15$ K
EG				
0.01	0.07	0.05	0.05	0.03
0.03	0.31	0.36	0.39	0.45
0.05	0.70	0.70	0.70	0.70
DEG				
0.01	0.16	0.12	0.14	0.39
0.03	0.63	0.46	0.78	0.84
0.05	0.79	0.87	1.22	1.24
TEG				
0.01	0.09	0.08	0.17	0.12
0.03	0.58	0.43	0.62	0.50
0.05	1.02	0.79	1.01	0.83

^a m_B is the molality of aqueous solutions of glycerol.

Table 4.4

Values of empirical parameters of equation 4.4 for glycols in aqueous glycerol solutions.

${}^a m_B$ (mol·kg ⁻¹)	$a \times 10^6$ (m ³ ·mol ⁻¹)	$b \times 10^6$ (m ³ ·mol ⁻¹ ·K ⁻¹)	$c \times 10^6$ (m ³ ·mol ⁻¹ ·K ⁻²)	R ²	ARD
EG					
0.00	53.66	0.046	-0.0004	0.9999	0.00005
0.01	53.71	0.044	-0.0004	0.9999	0.00005
0.03	54.01	0.054	-0.0002	0.9999	0.00012
0.05	54.36	0.045	-0.0002	0.9999	0.00010
DEG					
0.00	91.74	0.035	-0.0005	0.9999	0.00057
0.01	91.83	0.034	0.0024	0.9999	0.00073
0.03	92.31	0.043	0.0017	0.9999	0.00026
0.05	92.70	0.072	-0.0012	0.9999	0.00006
TEG					
0.00	128.53	0.054	0.0003	0.9999	0.00011
0.01	128.65	0.060	-0.0001	0.9999	0.00008
0.03	129.06	0.052	0.0006	0.9999	0.00039
0.05	129.45	0.045	0.0008	0.9999	0.00001

^a m_B is the molality of aqueous solutions of glycerol.

Table 4.5

Limiting apparent molar expansibilities, E_{ϕ}^o for glycols in aqueous glycerol solutions at different temperatures.

${}^a m_B (\text{mol} \cdot \text{kg}^{-1})$	$E_{\phi}^o \times 10^6 (\text{m}^3 \cdot \text{mol}^{-1} \cdot \text{K}^{-1})$				$(\partial E_{\phi}^o / \partial T)_p$ ($\text{m}^3 \cdot \text{mol}^{-1} \cdot \text{K}^{-2}$)
	$T= 293.15 \text{ K}$	$T= 298.15 \text{ K}$	$T= 303.15 \text{ K}$	$T= 308.15 \text{ K}$	
EG					
0.00	0.0494	0.0458	0.0423	0.0388	-0.0007
0.01	0.0476	0.0440	0.0405	0.0370	-0.0007
0.03	0.0561	0.0539	0.0518	0.0497	-0.0004
0.05	0.0470	0.0450	0.0430	0.0410	-0.0004
DEG					
0.00	0.0401	0.0348	0.0296	0.0244	-0.0010
0.01	0.0099	0.0340	0.0582	0.0824	0.0048
0.03	0.0261	0.0427	0.0593	0.0759	0.0033
0.05	0.0840	0.0720	0.0600	0.0481	-0.0024
TEG					
0.00	0.0510	0.0540	0.0570	0.0600	0.0006
0.01	0.0604	0.0595	0.0586	0.0577	-0.0002
0.03	0.0458	0.0519	0.0580	0.0641	0.0012
0.05	0.0370	0.0446	0.0521	0.0597	0.0015

${}^a m_B$ is the molality of aqueous solutions of glycerol.

Table 4.6

Values of ultrasonic speed, c , and apparent molar isentropic compression, $K_{\phi,s}$ of glycols in aqueous solutions of glycerol at different temperatures and experimental pressure, $p = 0.1$ MPa.

$^a m_A$ (mol·kg ⁻¹)	c (m·s ⁻¹)						$K_{\phi,s} \times 10^6$ (m ³ ·mol ⁻¹ ·GPa ⁻¹)					
	$T=293.15$ K	$T=298.15$ K	$T=303.15$ K	$T=308.15$ K	$T=293.15$ K	$T=298.15$ K	$T=303.15$ K	$T=308.15$ K	$T=293.15$ K	$T=298.15$ K	$T=303.15$ K	$T=308.15$ K
<i>EG + 0.00 mol·kg⁻¹ Glycerol</i>												
0.00000	1482.3	1495.9	1508.5	1519.1								
0.09889	1485.3	1498.9	1511.1	1521.8	-45.16	-44.28	-43.52	-42.93				
0.19894	1488.3	1501.7	1513.8	1524.0	-45.43	-44.54	-43.78	-43.18				
0.29967	1491.2	1504.3	1516.2	1526.2	-45.55	-44.65	-43.88	-43.29				
0.39481	1493.9	1506.6	1518.7	1528.3	-45.62	-44.72	-43.95	-43.35				
0.50155	1496.8	1509.1	1521.2	1530.3	-45.68	-44.78	-44.01	-43.41				
<i>EG + 0.01 mol·kg⁻¹ Glycerol</i>												
0.00000	1483.2	1497.0	1509.3	1519.9								
0.09871	1486.3	1500.1	1512.0	1522.6	-45.07	-44.24	-43.52	-42.91				
0.20179	1489.0	1502.5	1514.4	1524.6	-45.31	-44.48	-43.75	-43.14				
0.30048	1491.9	1505.0	1516.8	1526.8	-45.42	-44.59	-43.86	-43.25				
0.40056	1494.2	1507.2	1519.0	1528.8	-45.49	-44.65	-43.92	-43.31				
0.49986	1497.2	1509.7	1521.6	1530.9	-45.55	-44.71	-43.98	-43.36				
<i>EG + 0.03 mol·kg⁻¹ Glycerol</i>												

0.00000	1484.0	1497.8	1510.0	1520.6					
0.09813	1486.8	1500.6	1512.5	1523.0	-44.99	-44.16	-43.44	-42.84	
0.19827	1489.8	1503.1	1515.0	1525.2	-45.26	-44.42	-43.70	-43.09	
0.30069	1492.5	1505.7	1517.4	1527.4	-45.37	-44.53	-43.81	-43.20	
0.39774	1495.4	1508.3	1519.8	1529.6	-45.44	-44.60	-43.88	-43.26	
0.49630	1497.9	1510.7	1522.2	1531.6	-45.49	-44.65	-43.93	-43.32	
<i>EG + 0.05 mol·kg⁻¹ Glycerol</i>									
0.00000	1484.8	1498.6	1510.7	1521.2					
0.09871	1487.7	1501.3	1513.2	1523.5	-44.94	-44.11	-43.41	-42.80	
0.20179	1490.6	1504.0	1515.8	1525.9	-45.21	-44.38	-43.67	-43.06	
0.30048	1493.5	1506.6	1518.2	1528.2	-45.32	-44.48	-43.77	-43.16	
0.40056	1496.3	1509.4	1520.8	1530.5	-45.39	-44.55	-43.84	-43.23	
0.49986	1499.0	1511.7	1522.9	1532.5	-45.44	-44.61	-43.89	-43.28	
<i>DEG + 0.00 mol·kg⁻¹ Glycerol</i>									
0.00000	1482.3	1495.9	1508.5	1519.1					
0.09849	1487.7	1501.2	1513.1	1523.5	-45.19	-44.30	-43.54	-42.95	
0.19736	1493.1	1506.0	1517.6	1527.5	-45.49	-44.59	-43.83	-43.23	
0.29505	1498.1	1510.8	1522.0	1531.5	-45.62	-44.72	-43.95	-43.36	
0.41013	1504.1	1516.2	1526.9	1536.1	-45.73	-44.83	-44.06	-43.46	
0.50063	1508.3	1520.3	1530.6	1541.6	-45.81	-44.90	-44.13	-43.53	
<i>DEG + 0.01 mol·kg⁻¹ Glycerol</i>									

0.00000	1483.2	1497.0	1509.3	1519.9				
0.09949	1488.5	1502.0	1513.9	1524.2	-45.07	-44.24	-43.52	-42.91
0.19890	1493.9	1506.7	1518.3	1528.2	-45.36	-44.53	-43.80	-43.19
0.31059	1499.6	1512.2	1523.3	1532.7	-45.51	-44.67	-43.94	-43.33
0.38936	1503.7	1515.8	1526.6	1535.9	-45.59	-44.74	-44.02	-43.40
0.50142	1509.2	1521.0	1531.4	1540.3	-45.68	-44.83	-44.10	-43.48
<i>DEG + 0.03 mol·kg⁻¹ Glycerol</i>								
0.00000	1484.0	1497.8	1510.0	1520.6				
0.10019	1489.3	1502.7	1514.6	1524.8	-45.03	-44.20	-43.48	-42.87
0.19894	1494.5	1507.5	1519.0	1528.9	-45.31	-44.48	-43.75	-43.15
0.28890	1499.2	1511.8	1523.0	1532.5	-45.44	-44.60	-43.87	-43.26
0.39933	1504.7	1517.0	1527.7	1536.9	-45.54	-44.70	-43.97	-43.36
0.50046	1509.8	1521.6	1532.0	1540.8	-45.62	-44.78	-44.05	-43.44
<i>DEG + 0.05 mol·kg⁻¹ Glycerol</i>								
0.00000	1484.8	1498.6	1510.7	1521.2				
0.09939	1490.0	1503.4	1515.3	1525.5	-45.24	-44.14	-43.43	-42.83
0.19981	1495.2	1508.2	1519.6	1529.5	-45.53	-44.43	-43.71	-43.11
0.29813	1500.3	1512.8	1523.9	1533.5	-45.67	-44.56	-43.84	-43.23
0.40035	1505.3	1517.6	1528.3	1537.5	-45.77	-44.65	-43.93	-43.32
0.50015	1510.3	1522.1	1532.4	1541.3	-45.85	-44.73	-44.01	-43.40
<i>TEG + 0.00 mol·kg⁻¹ Glycerol</i>								

0.00000	1482.3	1495.9	1508.5	1519.1					
0.09650	1489.9	1503.5	1514.9	1525.1	-45.21	-44.33	-43.56	-42.97	
0.20020	1498.0	1511.0	1521.8	1531.3	-45.56	-44.66	-43.89	-43.30	
0.29205	1504.8	1517.6	1528.0	1536.9	-45.71	-44.82	-44.04	-43.45	
0.39856	1513.1	1525.4	1535.1	1543.3	-45.85	-44.95	-44.17	-43.57	
0.49879	1520.5	1532.2	1541.7	1550.9	-45.96	-45.05	-44.28	-43.68	
<i>TEG + 0.01 mol·kg⁻¹ Glycerol</i>									
0.00000	1483.2	1497.0	1509.3	1519.9					
0.09918	1491.3	1504.4	1515.8	1526.1	-45.10	-44.27	-43.55	-42.94	
0.20037	1499.2	1511.7	1522.6	1532.2	-45.43	-44.60	-43.87	-43.26	
0.30083	1506.6	1519.0	1529.4	1538.4	-45.60	-44.76	-44.03	-43.41	
0.40057	1514.4	1526.3	1536.0	1544.4	-45.72	-44.88	-44.15	-43.53	
0.49903	1521.8	1532.9	1542.5	1550.5	-45.83	-44.98	-44.25	-43.63	
<i>TEG + 0.03 mol·kg⁻¹ Glycerol</i>									
0.00000	1484.0	1497.8	1510.0	1520.6					
0.09994	1492.8	1505.4	1517.1	1527.1	-45.06	-44.23	-43.51	-42.91	
0.20031	1500.4	1512.7	1523.8	1533.2	-45.38	-44.54	-43.82	-43.21	
0.29980	1507.9	1519.9	1530.4	1539.4	-45.54	-44.70	-43.98	-43.37	
0.39952	1515.6	1527.1	1537.1	1545.4	-45.67	-44.83	-44.10	-43.49	
0.50056	1523.2	1534.0	1543.5	1551.5	-45.78	-44.93	-44.21	-43.59	
<i>TEG + 0.05 mol·kg⁻¹ Glycerol</i>									

0.00000	1484.8	1498.6	1510.7	1521.2				
0.10034	1493.1	1506.2	1518.1	1527.8	-45.01	-44.18	-43.47	-42.87
0.20070	1501.2	1513.5	1524.8	1534.0	-45.33	-44.50	-43.78	-43.18
0.29991	1509.3	1520.7	1531.3	1540.2	-45.49	-44.66	-43.94	-43.33
0.39955	1517.0	1527.9	1537.9	1546.2	-45.62	-44.77	-44.06	-43.45
0.50015	1524.4	1535.0	1544.3	1552.4	-45.73	-44.88	-44.16	-43.55

^a m_A is the molality of glycols in aqueous glycerol solutions; Standard uncertainties u are $u_r(m) = 1\%$, $u(T) = 0.001\text{ K}$, $u(c) = 1.0\text{ m}\cdot\text{s}^{-1}$ and $u(p) = 0.01\text{ MPa}$.

Table 4.7

Limiting apparent molar isentropic compression, $K_{\phi,s}^0$ and experimental slope, S_K^* for glycols in aqueous solutions of glycerol at different temperatures.

${}^a m_B$ (mol·kg ⁻¹)	$K_{\phi,s}^0 \times 10^6$ (m ³ ·mol ⁻¹ ·GPa ⁻¹)				$S_K^* \times 10^6$ (kg·m ³ ·mol ⁻² ·GPa ⁻¹)			
	T= 293.15 K	T= 298.15 K	T= 303.15 K	T= 308.15 K	T= 293.15 K	T= 298.15 K	T= 303.15 K	T= 308.15 K
EG								
0.00	-45.13(±0.08)	-44.23(±0.08)	-43.48(±0.08)	-42.88(±0.08)	-1.20(±0.24)	-1.19(±0.24)	-1.15(±0.23)	-1.15(±0.23)
0.01	-45.02(±0.07)	-44.19(±0.07)	-43.47(±0.07)	-42.87(±0.07)	-1.17(±0.22)	-1.13(±0.22)	-1.11(±0.22)	-1.09(±0.21)
0.03	-44.95(±0.08)	-44.12(±0.08)	-43.41(±0.08)	-42.81(±0.08)	-1.98(±0.25)	-1.17(±0.24)	-1.14(±0.24)	-1.12(±0.24)
0.05	-44.91(±0.08)	-44.08(±0.08)	-43.37(±0.08)	-42.77(±0.08)	-1.94(±0.24)	-1.14(±0.24)	-1.11(±0.24)	-1.09(±0.24)
DEG								
0.00	-45.13(±0.08)	-44.25(±0.08)	-43.49(±0.08)	-42.90(±0.08)	-1.45(±0.24)	-1.40(±0.24)	-1.38(±0.24)	-1.36(±0.24)
0.01	-45.01(±0.08)	-44.18(±0.08)	-43.46(±0.08)	-42.85(±0.08)	-1.46(±0.24)	-1.41(±0.24)	-1.38(±0.24)	-1.37(±0.24)
0.03	-44.97(±0.08)	-44.14(±0.08)	-43.42(±0.08)	-42.82(±0.08)	-1.42(±0.24)	-1.38(±0.24)	-1.35(±0.23)	-1.34(±0.23)
0.05	-45.18(±0.08)	-44.09(±0.08)	-43.38(±0.08)	-42.78(±0.08)	-1.44(±0.24)	-1.39(±0.24)	-1.36(±0.23)	-1.34(±0.23)
TEG								
0.00	-45.13(±0.09)	-44.25(±0.09)	-43.48(±0.08)	-42.90(±0.08)	-1.77(±0.26)	-1.73(±0.26)	-1.70(±0.25)	-1.68(±0.25)
0.01	-45.01(±0.08)	-44.19(±0.08)	-43.47(±0.08)	-42.86(±0.08)	-1.74(±0.25)	-1.70(±0.24)	-1.68(±0.24)	-1.65(±0.24)
0.03	-44.97(±0.08)	-44.14(±0.08)	-43.42(±0.08)	-42.82(±0.08)	-1.72(±0.24)	-1.68(±0.24)	-1.67(±0.23)	-1.64(±0.23)
0.05	-44.92(±0.08)	-44.10(±0.08)	-43.39(±0.08)	-42.79(±0.08)	-1.72(±0.24)	-1.68(±0.24)	-1.66(±0.23)	-1.63(±0.23)

${}^a m_B$ is the molality of aqueous solutions of glycerol.

Table 4.8

Partial molar isentropic compression of transfer, $\Delta K_{\phi,s}^0$ of glycols in aqueous solution of glycerol at different temperatures.

${}^a m_B (\text{mol} \cdot \text{kg}^{-1})$	$\Delta K_{\phi,s}^0 \times 10^6 (\text{m}^3 \cdot \text{mol}^{-1} \cdot \text{GPa}^{-1})$			
	$T= 293.15 \text{ K}$	$T= 298.15 \text{ K}$	$T= 303.15 \text{ K}$	$T= 308.15 \text{ K}$
EG				
0.01	0.10	0.04	0.00	0.02
0.03	0.17	0.11	0.07	0.08
0.05	0.22	0.15	0.10	0.11
DEG				
0.01	0.13	0.07	0.03	0.05
0.03	0.17	0.11	0.06	0.08
0.05	-0.05	0.16	0.11	0.12
TEG				
0.01	0.12	0.06	0.02	0.04
0.03	0.16	0.10	0.06	0.07
0.05	0.21	0.15	0.10	0.11

${}^a m_B$ is the molality of aqueous solutions of glycerol.

Table 4.9

Pair and triplet interaction coefficient of glycols in aqueous solutions of glycerol at different temperatures.

T (K)	$V_{AB} \times 10^6$ ($\text{m}^3 \cdot \text{mol}^{-2} \cdot \text{kg}$)	$V_{ABB} \times 10^6$ ($\text{m}^3 \cdot \text{mol}^{-3} \cdot \text{kg}^2$)	$K_{AB} \times 10^6$ ($\text{m}^3 \cdot \text{mol}^{-2} \cdot \text{kg} \cdot \text{GPa}^{-1}$)	$K_{ABB} \times 10^6$ ($\text{m}^3 \cdot \text{mol}^{-3} \cdot \text{kg}^2 \cdot \text{GPa}^{-1}$)
EG				
293.15	2.41	61.81	4.60	-32.66
298.15	3.33	49.30	2.21	-9.07
303.15	4.40	35.21	0.88	2.37
308.15	5.59	20.96	1.28	-2.47
DEG				
293.15	12.38	-58.28	7.74	-109.93
298.15	5.82	39.22	2.65	-14.32
303.15	11.54	10.92	1.16	-0.98
308.15	17.87	-74.87	1.82	-8.48
TEG				
293.15	6.90	45.18	4.62	-34.12
298.15	5.15	37.19	2.44	-12.83
303.15	9.95	2.95	0.99	0.04
308.15	7.67	8.77	1.60	-6.85

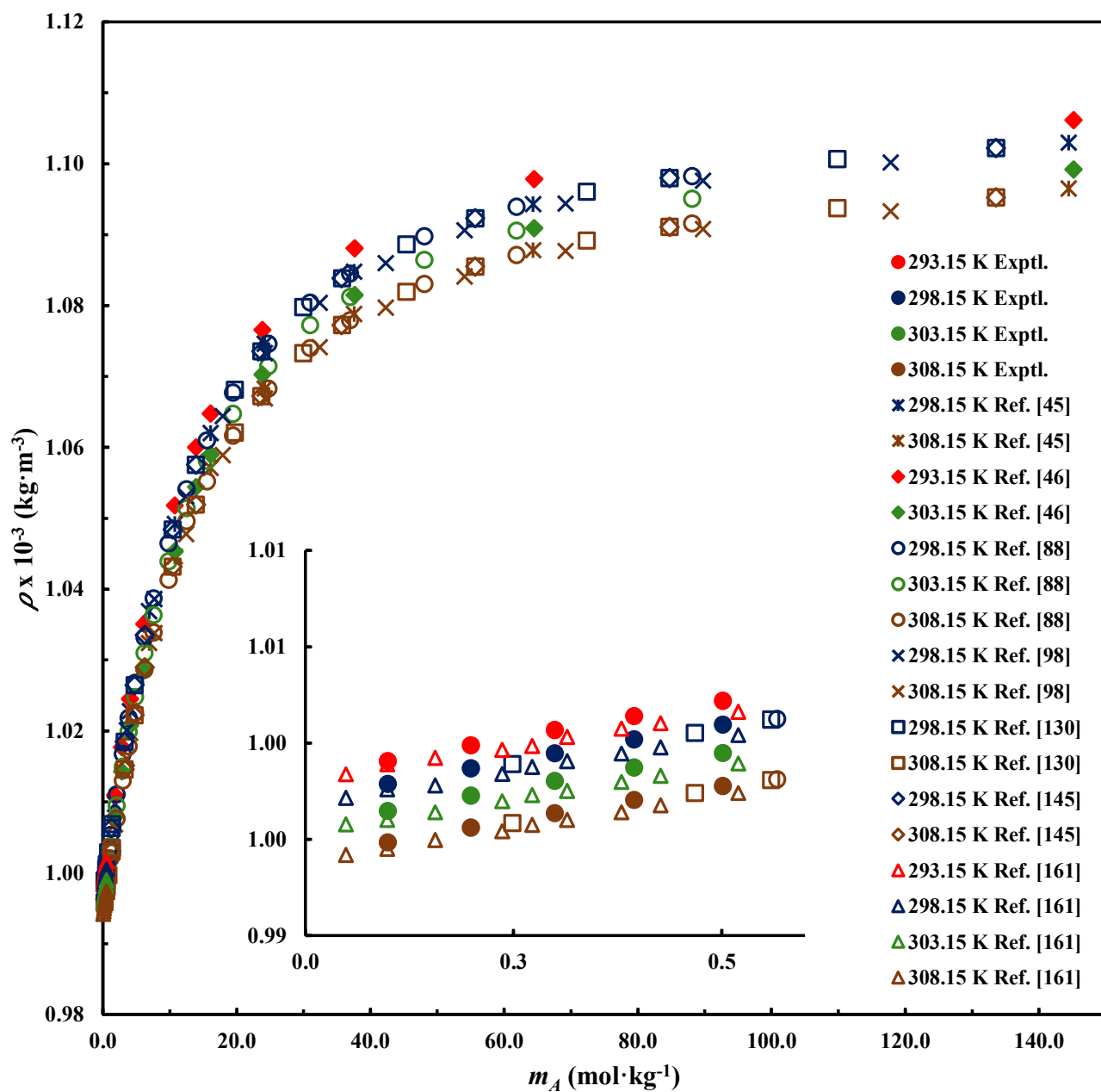


Figure 4.1: Plots of experimental and literature values [45, 46, 88, 98, 130, 145, 161] of densities for (ethylene glycol + water) mixtures at different temperatures.

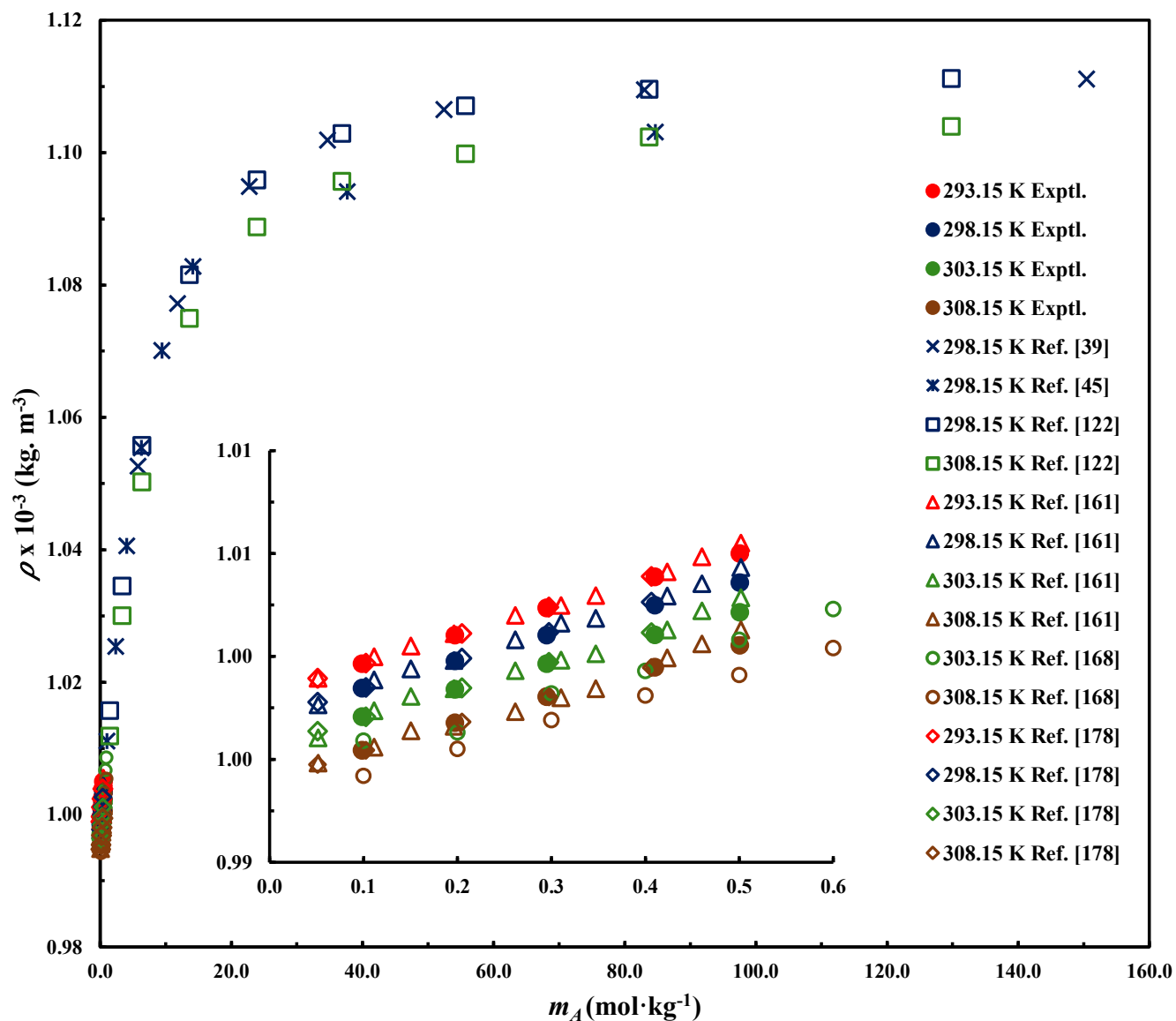


Figure 4.2: Plots of experimental and literature values [39, 45, 122, 161, 168, 178] of densities for (diethylene glycol + water) mixtures at different temperatures.

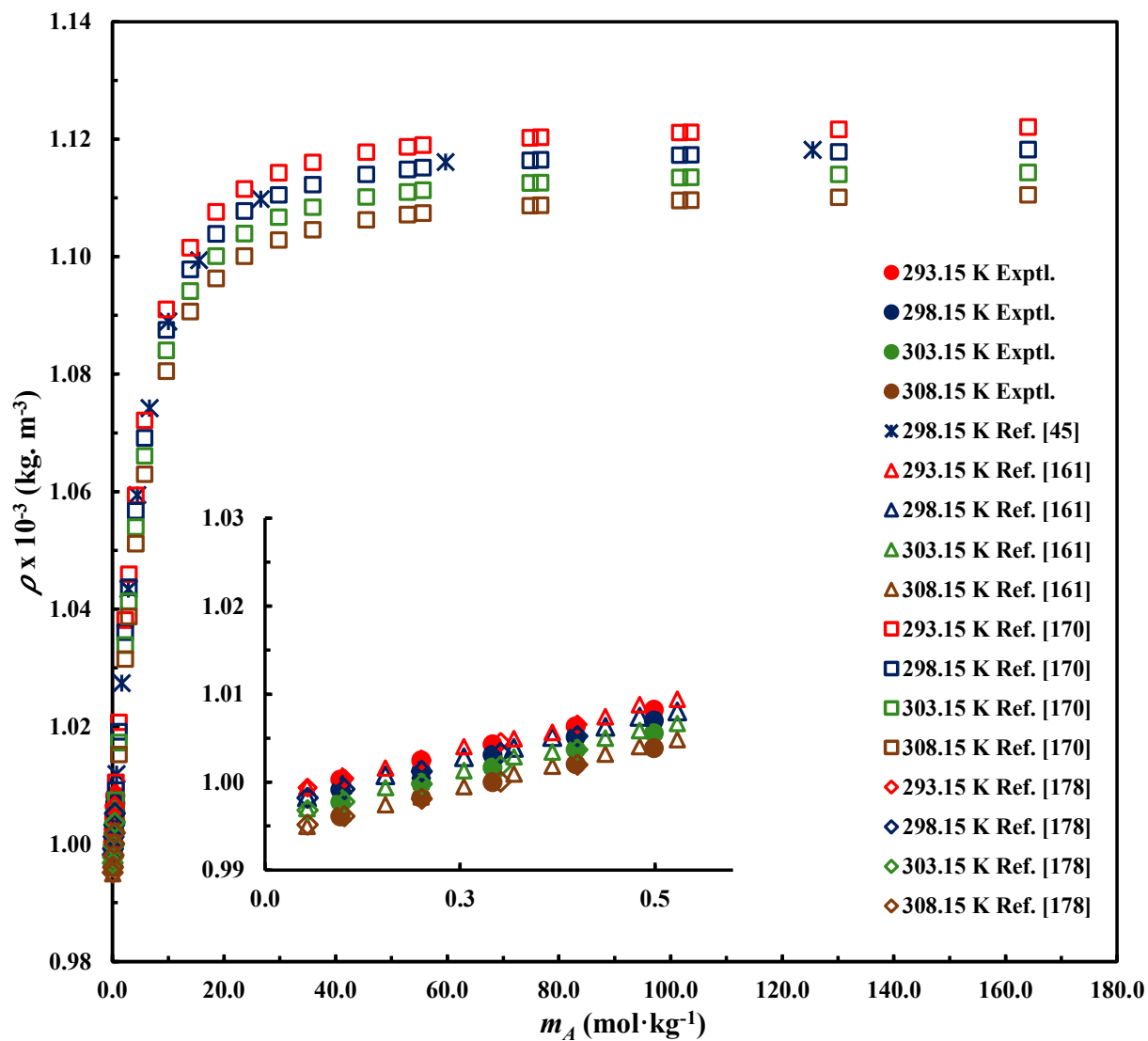


Figure 4.3: Plots of experimental and literature values [45, 161, 170, 178] of densities for (triethylene glycol + water) mixtures at different temperatures.

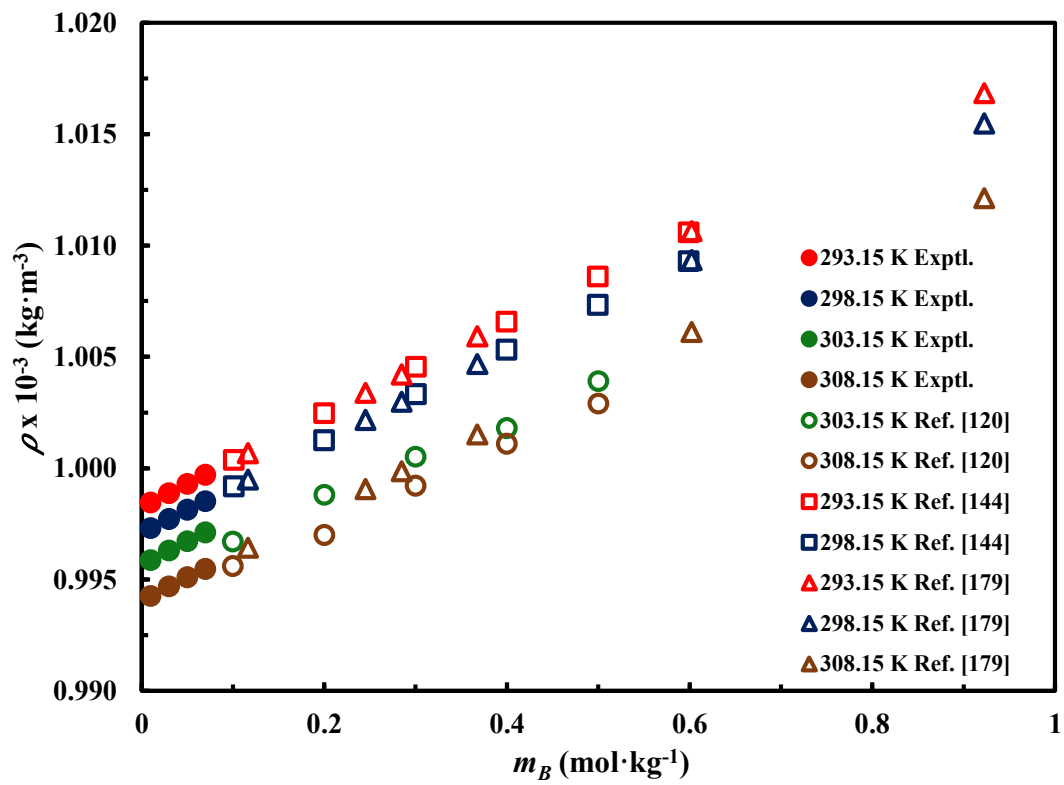


Figure 4.4: Plots of experimental and literature values [120, 144, 179] of densities for (glycerol + water) mixtures at 298.15 K.

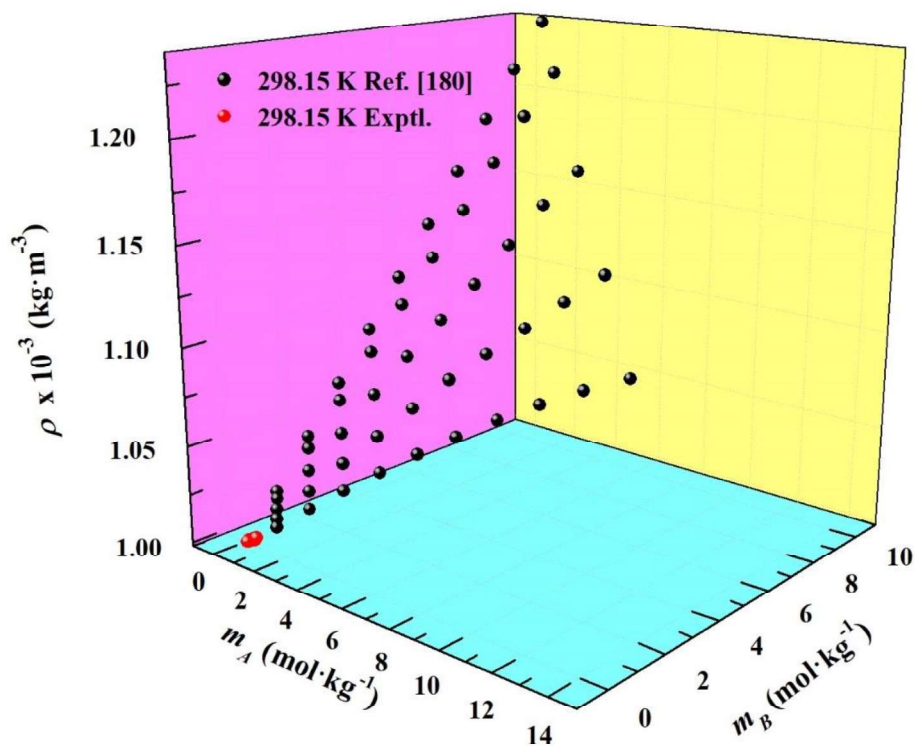


Figure 4.5: Plots of experimental and literature values of densities for ethylene glycol in different concentrations of aqueous glycerol solutions at 298.15 K.

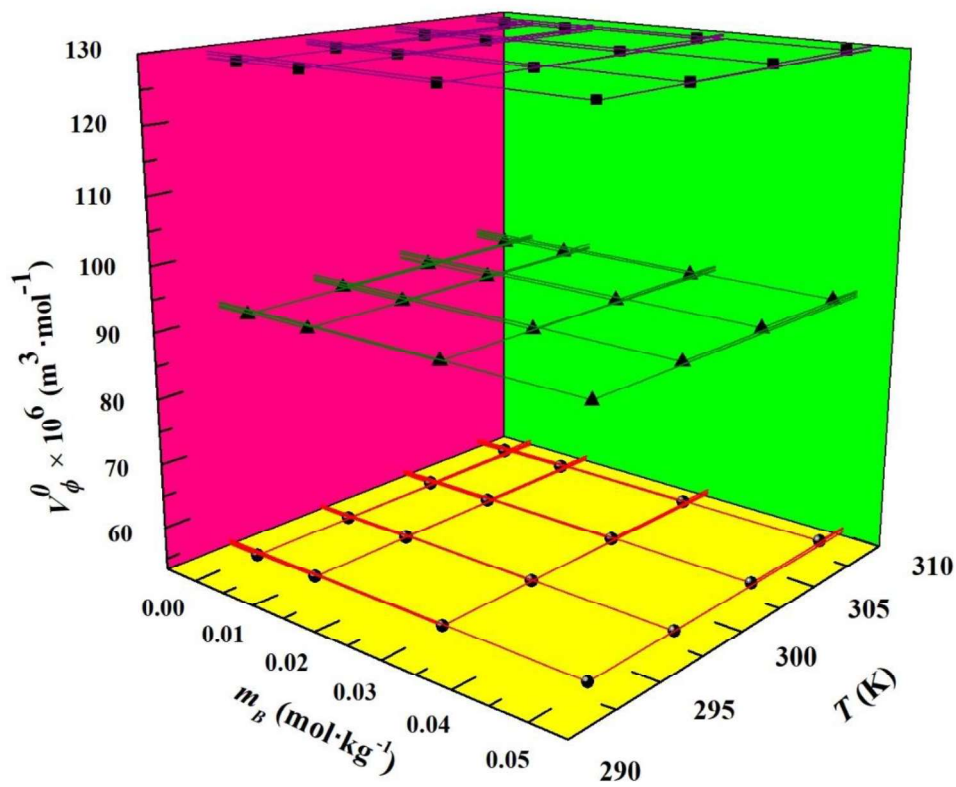


Figure 4.6: Plots of partial molar volume V_ϕ^o for ethylene glycol (●), diethylene glycol (▲) and triethylene glycol (■) in different concentrations of aqueous glycerol solutions at different temperatures.

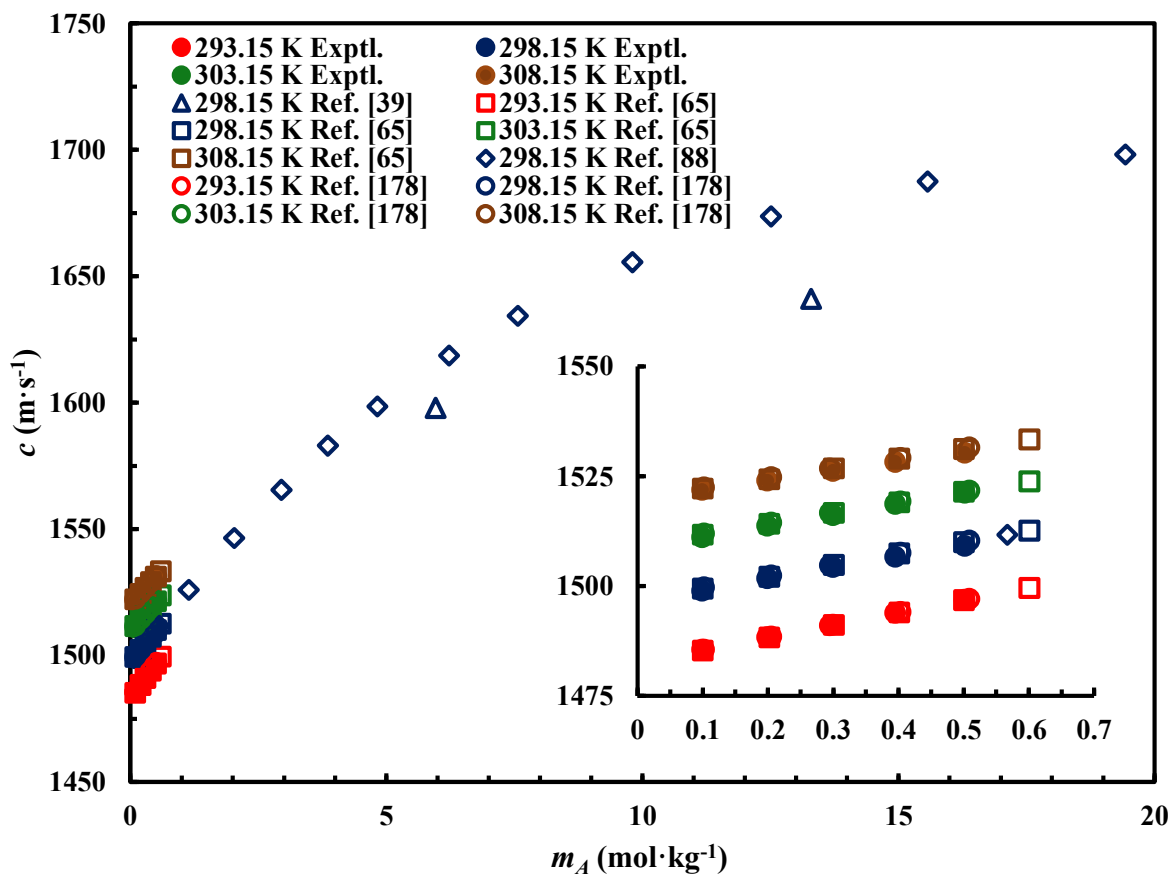


Figure 4.7: Plots of experimental and literature values [39, 65, 88, 178] of ultrasonic speeds for (ethylene glycol + water) mixtures at different temperatures.

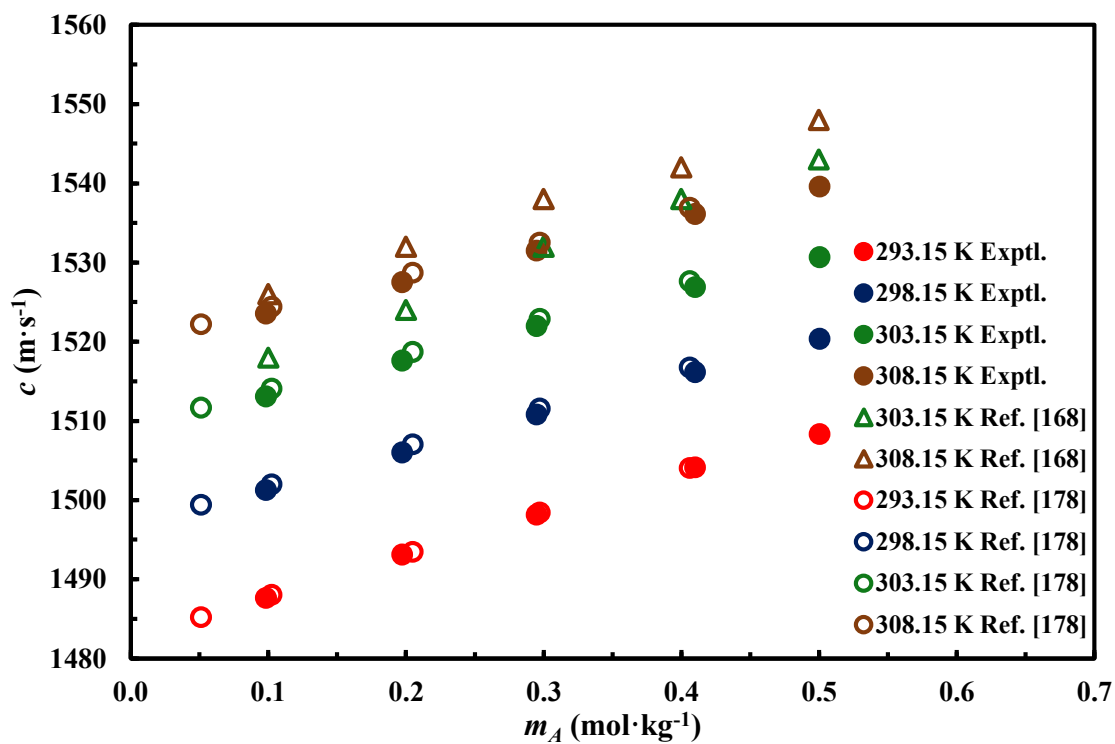


Figure 4.8: Plots of experimental and literature values [168, 178] of ultrasonic speeds for (diethylene glycol + water) mixtures at different temperatures.

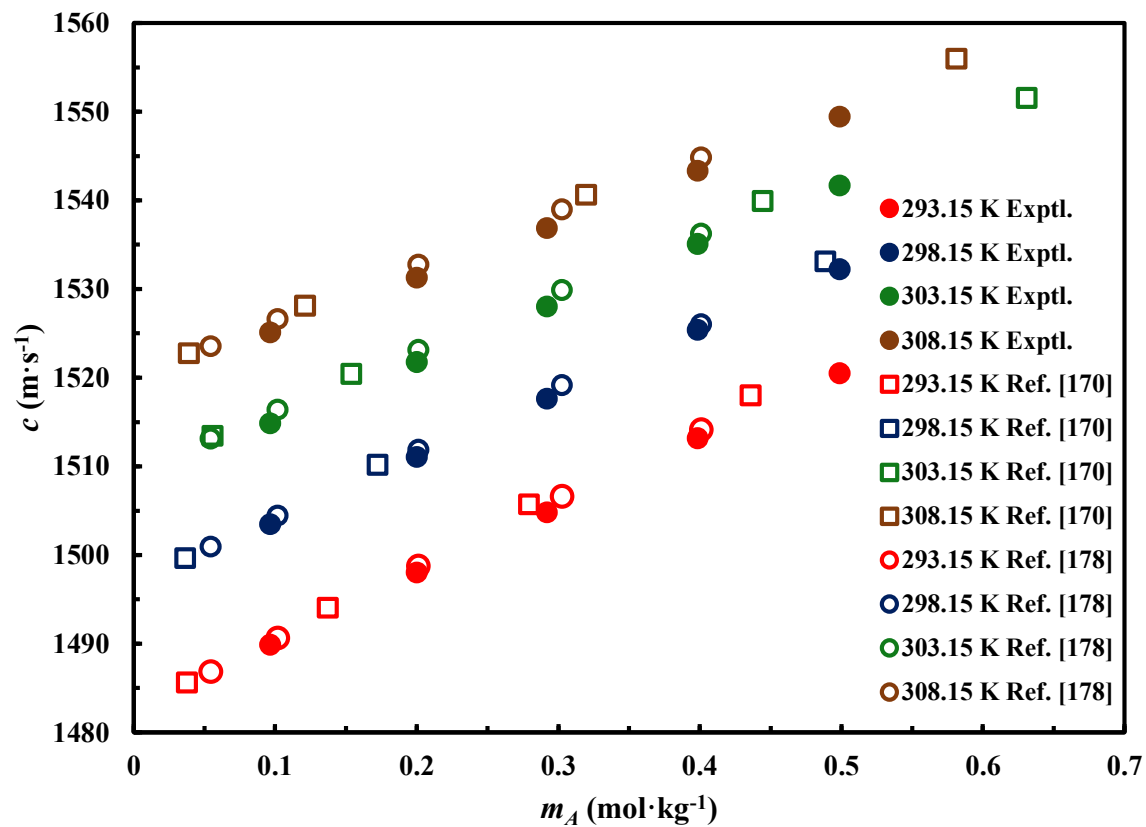


Figure 4.9: Plots of experimental and literature values [170, 178] of ultrasonic speeds for (triethylene glycol + water) mixtures at different temperatures.

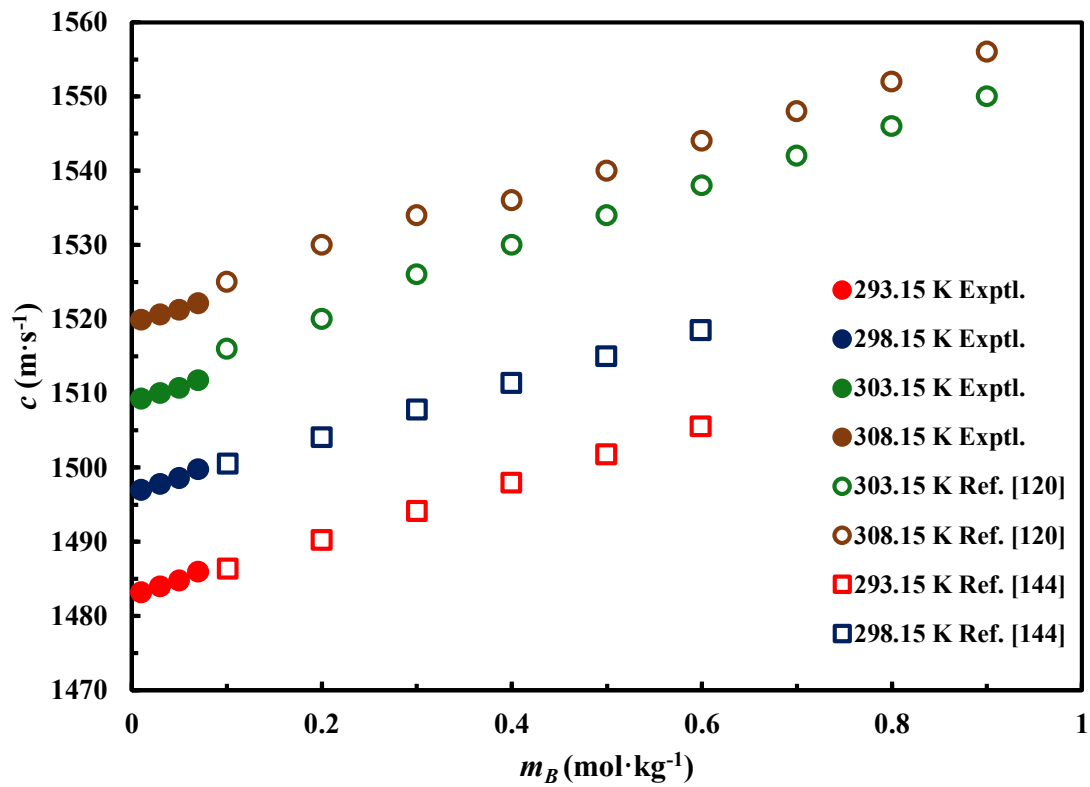


Figure 4.10: Plots of experimental and literature values [120, 144] of ultrasonic speeds for (glycerol + water) mixtures at 298.15 K.

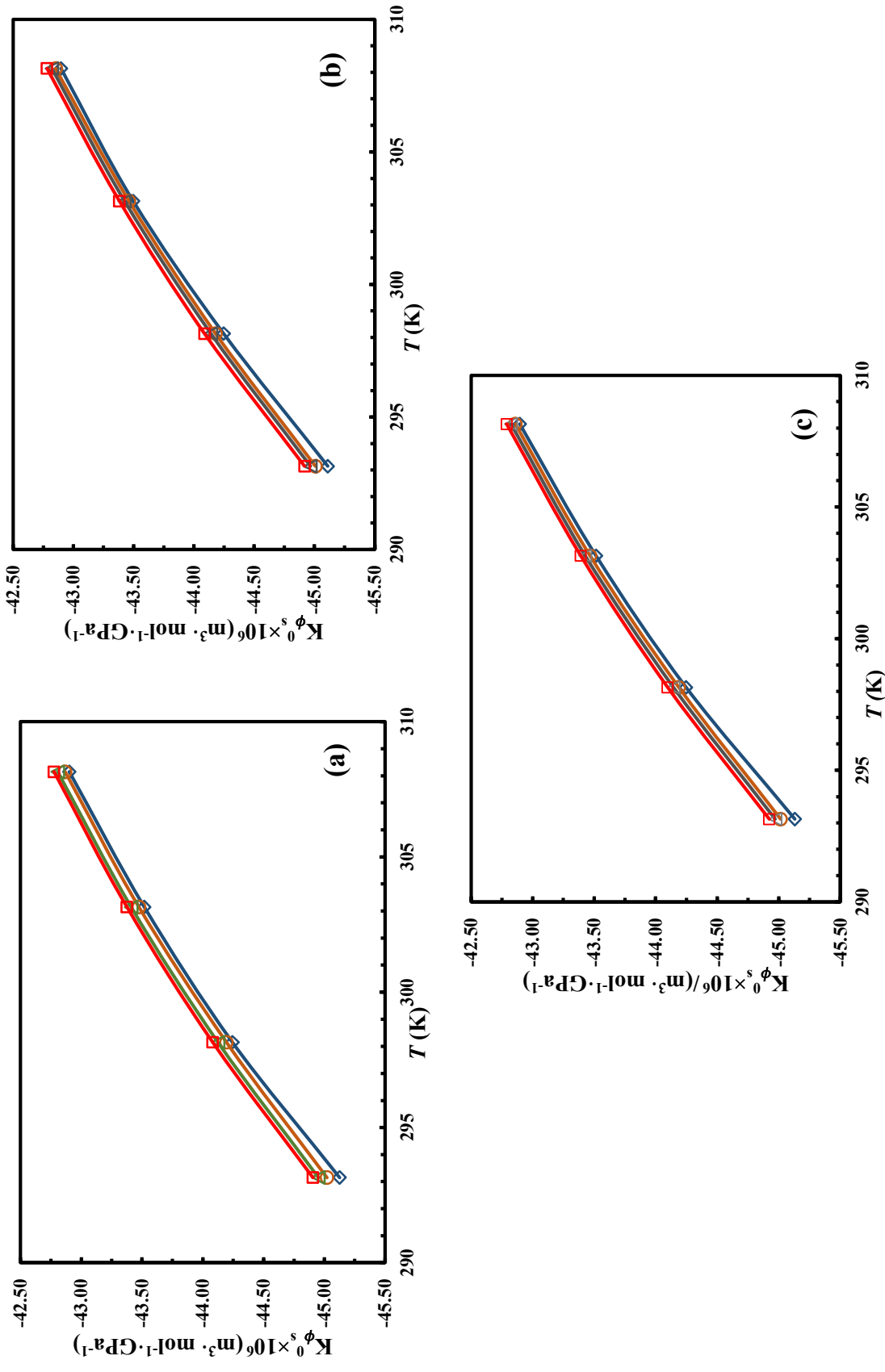


Figure 4.11: Partial molar isentropic compression K_ϕ^0 for (a) ethylene glycol (b) diethylene glycol (c) triethylene glycol in (\diamond , 0.00 mol·kg⁻¹; \circ , 0.01 mol·kg⁻¹; Δ , 0.03 mol·kg⁻¹; \square , 0.05 mol·kg⁻¹) aqueous glycerol solutions at different temperatures.

Section II

In previous section, we have reported the densities, ρ and speed of sound, c of ethylene glycol (EG), diethylene glycol (DEG) and triethylene glycol (TEG) in (0.00, 0.01, 0.03, 0.05) mol·kg⁻¹ aqueous solutions of glycerol at temperatures $T = (293.15, 298.15, 303.15, 308.15)$ K. In continuation of our work on glycols, in this section we have reported the densities and speed of sound for PEG-400 and PEG-4000 in (0.00, 0.01, 0.03, 0.05, 0.07) mol·kg⁻¹ aqueous solutions of glycerol at temperatures $T = (293.15, 298.15, 303.15, 308.15)$ K.

Density

The experimental densities, ρ for PEG-400 and PEG-4000 in (0.00, 0.01, 0.03, 0.05, 0.07) mol·kg⁻¹ aqueous solutions of glycerol were measured at temperatures $T = (293.15, 298.15, 303.15, 308.15)$ K and are indexed in Table 4.10. It has been professed from data that the density values are rising with respect to concentration of PEGs and as well as glycerol. But at a specific concentration of glycerol, the density values are falling relating to temperature. The experimental density values for aqueous PEGs solutions at different temperatures have been compared with literature values [95, 118, 200 and 201] and the comparison is shown by graph in Figure 4.12 and 4.13. From the Figures 4.12 and 4.13, it is clear that the experimental values are in coherence with literature values. The comparison for the densities of liquid mixtures (glycerol + water) has also been done with the literature values [120, 144 and 179] and is represented in Figure 4.14. The experimental densities are found to be in trend with the literature values given in reference [144 and 179] but a little deviation has been observed from the values reported in reference [120] at temperature 303.15 K and 308.15 K.

Apparent molar volume

The experimental densities are used to compute the apparent molar volumes (V_ϕ) utilizing equation 4.1. The computed apparent molar volumes are attributed in Table 4.10 and all the values are found to be positive. With rising concentration of glycerol, the V_ϕ values

tend to increase. Also, at a specific concentration of glycerol, the upsurge in values of V_ϕ is noticed with regard to upsurge in molality of PEGs and temperature which infers pronounced solute-solvent interactions. The surge in V_ϕ values is also perceived in relation with molar mass of PEGs that is with escalating molar mass of PEGs the apparent molar volumes also escalate at entire temperature range and for entire glycerol's concentrations ensuing extremum solute-solvent interaction in PEG-4000 as shown in Scheme 1. This enhancement in V_ϕ values can be accredited to various factors namely hydrophilic effect, hydrophobic hydration in water-rich region, forces such as dipole-dipole and dipole-induced dipole interactions [146].

Partial molar volume

By the means of least squares fitting of apparent molar volume V_ϕ , partial molar volume V_ϕ^0 is calculated from equation 4.2. The values of V_ϕ^0 and S_V^* along with standard errors computed by least squares fitting of V_ϕ values to equation 4.2, are collected in Table 4.11. The entire values of V_ϕ^0 are positive and rise with rise in temperature and concentration of glycerol in both PEGs as represented in Figure 4.15. Further at individual temperature, the values of V_ϕ^0 upsurge with respect to molar mass of PEGs resulting in highest values for PEG-4000 which further intimates intensified solute-solvent interactions for PEG-4000 as compared to PEG-400. This surge in V_ϕ^0 values can be accredited to strong hydrogen bond interactions among the oxygen atoms of PEGs and hydrogen atoms of water. The packaging effects (upon mixing, the comparatively trivial water molecules fit into the free volume available for PEGs) also contributes to rising V_ϕ^0 values [200]. From the definition, the partial molar volumes are independent of solute-solute interaction, hence delivers information regarding solute-solvent interactions [202]. The variation in V_ϕ^0 values of PEG-400 and PEG-4000 is very high which acclaims that interaction among unlike molecules is dreadfully susceptible by the size of hydrocarbon chain [91]. Furthermore, from Table 4.11, the magnitude of S_V^* for whole concentrations of glycerol and at whole temperature range has been perceived positive. The solute-solute interactions in the solutions of PEGs

in glycerol are manifested from the positive S_V^* values. But no regular trend has been obtained for S_V^* values which recommends the predominance of solute-solvent interactions over solute-solute interactions. The irregular trend in values of S_V^* indicates that solute-solute interactions are affected by some other factors also [182].

Partial molar volume of transfer

At infinite dilution, the transfer volumes of PEGs from water to aqueous glycerol solutions have been calculated from equation 4.3. The evaluated values of ΔV_ϕ^0 are indexed in Table 4.12. The positive ΔV_ϕ^0 values are observed for all PEGs and are rising with rise in concentration of glycerol which deduces enormous desiccation results on PEGs. Relating to increasing temperature, no steady trend has been observed in ΔV_ϕ^0 values. Regarding the pure water's structure, the occurrence of a structural network of water along with relatively large empty areas – clathrates which can be infiltrated by diverse molecules, is presumed through the models defined by Pauling [183, 184]. Perhaps very insignificant amount of PEG molecules can be located in the crates of the water structures consequently not to eradicate the cage structure. Relatively higher content of PEGs abolishes a cage structure and as a result of hydrogen bond formation among organic molecules and water, new structures are formed [170]. Moreover, the positive transfer volumes infer structure making/promoting ability of solutes as the structural moiety of glycerol and PEG contains polar group.

Temperature dependent partial molar volume

By the means of general polynomial equation, the change in apparent molar volumes with the temperature at infinite dilution can be uttered as equation 4.4. In aqueous glycerol, the values of these constants for PEG-400 and PEG-4000 are reported in Table 4. These parameters are used to analyze V_ϕ^0 and deviations achieved from computed and experimental values are also listed in Table 4.13. The deviations are evaluated from the equation 4.5. The values incorporated in Table 4.13 for deviations are very small that fits

into the polynomial equation very magnificently which is manifested from R^2 values in the existing study.

The temperature dependence at infinite dilution of partial molar volume (V_ϕ^0) can be articulated in terms of absolute temperature (T) by equation 4.6. The similar equation 4.6 is used to estimate partial molar expansibilities. The limiting apparent molar expansibility at infinite dilution, $E_\phi^0 = (\partial V_\phi^0 / \partial T)_p$ is well-thought-out to be a beneficial measure [185] of solute-solvent interaction prevailing in the solution. The general thermodynamic expression, given by Hepler [186] determined the structure making and breaking capability of the solute in solvent using the equation 4.7. The structure making and breaking ability of solute in solvent can be decided [186, 187] via sign of $(\partial E_\phi^0 / \partial T)_p$. The positive and minute negative values of $(\partial E_\phi^0 / \partial T)_p$ has been observed for structure making solutes whereas negative values of $(\partial E_\phi^0 / \partial T)_p$ are observed for solutes having structure breaking capacity. The partial molar expansibilities E_ϕ^0 and $(\partial E_\phi^0 / \partial T)_p$ are ascribed in Table 4.14. The values of limiting apparent molar expansibility are found to be positive at entire temperature range and concentrations of glycerol. The solute-solvent interactions are specified by the positive E_ϕ^0 values in the present ternary systems, as previously proposed by apparent molar volume statistics. The values of E_ϕ^0 show an asymmetrical trend with an upsurge in the temperature as well as in the concentration of glycerol solutions. The small negative and positive $(\partial E_\phi^0 / \partial T)_p$ values for the mixtures of PEGs recommend the structure making capability of PEGs in whole aqueous glycerol solutions.

Ultrasonic speed

The values of ultrasonic speed, c for PEG-400 and PEG-4000 in (0.00, 0.01, 0.03, 0.05, 0.07) mol·kg⁻¹ aqueous solutions of glycerol are determined at temperatures $T = (293.15, 298.15, 303.15, 308.15)$ K and are attributed in Table 4.15. The experimental ultrasonic speeds for (PEG-400 + water and PEG-4000 + water) have been compared with the literature values [118, 200] and are represented graphically in Figures 4.16 and 4.17 respectively. The obtained ultrasonic speeds for (glycerol + water) have also been compared with literature values [120, 144] and are represented in Figure 4.18. It is noticed

from Table 4.15 that the values of ultrasonic speed increase in order with respect to temperature as well as concentration of glycerol. This increase in ultrasonic speed values relating to temperature is characteristic for water and is concerned with the 3-dimensional network of hydrogen bonds in the structure of water [170]. The increase in ultrasonic speed in any solution suggests the greater connotation amidst the molecules of the solution. The greater connotation is due to intramolecular hydrogen bonding amongst solute molecules itself and intermolecular hydrogen bonds amid solute and solvent molecule [168]. Also, the ultrasonic speed escalates with upsurge in molality of PEGs for a specific concentration of glycerol, as the glycerol molecules interrelate positively with water to support H-bond network in solvent [145]. Further, while the addition of PEG to the solvent, hydrogen bonds among glycerol and water molecules get hampered and are demolished. Simultaneously, new hydrogen bonds among molecules of solvent (glycerol + water) and molecules of PEGs are designed [170].

Apparent molar isentropic compression

By the means of equation 4.8, the apparent molar isentropic compression for PEGs in aqueous and mixed aqueous solutions of glycerol at different temperatures, is evaluated. An isentropic compressibility has been evaluated from equation 4.9. The calculated values of $K_{\phi,s}$ for several molal concentrations (m_A) of PEG-400 and PEG-4000 in (0.00, 0.01, 0.03, 0.05, 0.07) mol·kg⁻¹ glycerol at different temperatures are described in Table 4.15. From the evaluated $K_{\phi,s}$ values, it is analyzed that the values are negative at entire concentrations of glycerol and at whole temperature range. These values of $K_{\phi,s}$ become less negative with rise in temperature and concentration of glycerol due to progress of system at larger temperatures but increasing molality of PEGs results in the more negative $K_{\phi,s}$ values. The negative $K_{\phi,s}$ values specify that the water molecules around solute are not as much compressible as the water molecules in the bulk solution [188, 189] resulting in the contraction of the water molecules around it as of hydrophobic interactions of a non-polar group. Consequently, the pressure on bulk water molecules fallouts in compressibility

of the solution, which additionally advocates the robust solute-solvent interactions among the molecules of PEGs and glycerol's molecules.

Partial molar isentropic compression

The partial molar isentropic compression ($K_{\phi,s}^o$) can be premeditated through detecting the change in apparent molar isentropic compression ($K_{\phi,s}$) along with molal concentration and is epitomized by equation 4.10. The S_K^* values altogether with standard errors derived by the method of least squares fitting and $K_{\phi,s}^o$ values are reported in Table 4.16. The lesser $K_{\phi,s}^o$ values for PEGs in aqueous glycerol solutions at greater temperatures indicate the release of some water molecules to the bulk. The values of $K_{\phi,s}^o$ tend to be more negative at lower temperatures as revealed in Figure 4.19, which points towards the strong attractive interactions amongst PEGs and water molecules [191]. No systematic trend is observed for variation of $K_{\phi,s}^o$ with glycerol concentration.

Partial molar isentropic compressions of transfer

For each PEG at infinite dilution, from water to aqueous glycerol solutions, the partial molar isentropic compressions of transfer ($\Delta K_{\phi,s}^o$) are evaluated from equation 4.11. The computed $\Delta K_{\phi,s}^o$ values are reported in Table 4.17. The positive and small negative values are observed for partial molar isentropic compression of transfer which intimates the predominance of interactions among PEGs and glycerol which further infers structure making tendency of ions. Thus, more negative values for $K_{\phi,s}^o$ and small negative and positive values for $\Delta K_{\phi,s}^o$ suggest the determined solute-solvent interactions and structure making capability of solute in the present ternary system.

Pair and triplet interaction coefficients

The pair and triplet interaction coefficients are computed based upon McMillan–Mayer theory [195] of liquid mixtures which allows the parting of effects because of interactions among the pairs of solute molecules and those owing to its interaction among above two

solute molecules. This theory was then further being discussed by Friedman and Krishnan [196] and Franks *et al.* [197] to facilitate solute-cosolute interactions in the solvation spheres. Therefore, partial molar volume of transfer and partial molar isentropic compression of transfer can be articulated as equations 4.12 and 4.13. The pair and triplet coefficients are symbolized by the corresponding parameters, for volume V_{AB} , V_{ABB} and for isentropic compression K_{AB} , K_{ABB} . Through fitting of ΔV_{ϕ}^0 and $\Delta K_{\phi,s}^0$ values to above equations, the values of constants (V_{AB} , V_{ABB} , K_{AB} and K_{ABB}) are computed and are detailed in Table 4.18. The pair interaction coefficients V_{AB} and K_{AB} are positive at all temperatures for both PEGs except for K_{AB} values for PEG-4000 at higher temperatures. The triplet interaction coefficient for volume V_{ABB} is negative for both PEGs at entire temperature range. Whereas, the triple interaction coefficient for isentropic compression K_{ABB} is negative for PEG-400 and positive for PEG-4000 at whole temperatures. The overall positive values for pair interaction coefficients V_{AB} and K_{AB} infers [199] the dominance of pair-wise interactions in the present ternary systems of PEGs-glycerol-water.

Table 4.10

Values of densities, ρ , and apparent molar volumes, V_ϕ of glycols in aqueous solutions of glycerol at different temperatures and experimental pressure, $p = 0.1$ MPa.

$^a m_A$ (mol·kg ⁻¹)	$\rho \times 10^3$ (kg·m ⁻³)					$V_\phi \times 10^6$ (m ³ ·mol ⁻¹)						
	$T=293.15$ K	$T=298.15$ K	$T=303.15$ K	$T=308.15$ K	$T=293.15$ K	$T=298.15$ K	$T=303.15$ K	$T=308.15$ K	$T=293.15$ K	$T=298.15$ K	$T=303.15$ K	$T=308.15$ K
<i>PEG-400 + 0.00 mol·kg⁻¹ Glycerol</i>												
0.00000	0.998211	0.997047	0.995656	0.994039					328.91	330.74	332.28	333.61
0.00498	0.998567	0.997395	0.995998	0.994377					329.55	331.37	332.86	334.34
0.01000	0.998918	0.997739	0.996337	0.994709					330.17	332.08	333.61	335.15
0.01499	0.999260	0.998072	0.996663	0.995030					330.82	332.78	334.29	335.91
0.01992	0.999589	0.998393	0.996979	0.995339					331.46	333.39	334.93	336.58
0.02453	0.999890	0.998687	0.997268	0.995621					332.22	334.26	335.76	337.45
0.03006	1.000242	0.999027	0.997603	0.995949					332.93	334.97	336.49	338.21
0.03525	1.000564	0.999340	0.997910	0.996249					333.61	335.65	337.21	338.89
0.03992	1.000846	0.999614	0.998176	0.996511								
<i>PEG-400 + 0.01 mol·kg⁻¹ Glycerol</i>												
0.00000	0.998452	0.997308	0.995869	0.994253					331.04	332.75	334.22	335.61
0.00508	0.998804	0.997653	0.996208	0.994587					331.69	333.37	334.84	336.19
0.01042	0.999166	0.998007	0.996557	0.994932					332.24	333.91	335.37	336.68
0.01501	0.999470	0.998306	0.996851	0.995222								

0.02069	0.999839	0.998667	0.997207	0.995573	332.92	334.58	336.02	337.35
0.02547	1.000142	0.998964	0.997499	0.995861	333.50	335.15	336.57	337.90
0.03014	1.000432	0.999249	0.997779	0.996138	334.05	335.69	337.11	338.42
0.03512	1.000735	0.999545	0.998071	0.996426	334.65	336.28	337.69	338.98
0.04056	1.001057	0.999862	0.998383	0.996734	335.31	336.92	338.31	339.59
<i>PEG-400 + 0.03 mol·kg⁻¹ Glycerol</i>								
0.00000	0.998865	0.997707	0.996304	0.994684				
0.00481	0.999187	0.998024	0.996617	0.994994	333.31	334.61	335.75	336.81
0.01017	0.999539	0.998371	0.996960	0.995333	333.82	335.08	336.31	337.45
0.01521	0.999864	0.998692	0.997275	0.995644	334.31	335.56	336.82	338.01
0.02019	1.000178	0.999003	0.997581	0.995947	334.81	336.02	337.31	338.49
0.02530	1.000496	0.999315	0.997889	0.996251	335.29	336.51	337.82	339.00
0.02990	1.000776	0.999592	0.998161	0.996520	335.74	336.95	338.29	339.46
0.03506	1.001085	0.999896	0.998460	0.996816	336.24	337.45	338.79	339.96
0.03928	1.001333	1.000141	0.998700	0.997053	336.65	337.84	339.21	340.37
<i>PEG-400 + 0.05 mol·kg⁻¹ Glycerol</i>								
0.00000	0.999290	0.998124	0.996720	0.995094				
0.00518	0.999622	0.998452	0.997044	0.995415	335.91	337.03	338.21	339.28
0.01004	0.999930	0.998756	0.997344	0.995712	336.24	337.35	338.55	339.62
0.01489	1.000232	0.999055	0.997639	0.996004	336.61	337.68	338.89	339.95

0.01992	1.000541	0.999360	0.997940	0.996302	336.95	338.05	339.24	340.33
0.02505	1.000852	0.999667	0.998243	0.996601	337.32	338.41	339.61	340.71
0.02994	1.001144	0.999955	0.998527	0.996882	337.66	338.75	339.94	341.05
0.03489	1.001434	1.000242	0.998812	0.997163	338.02	339.10	340.26	341.39
0.04101	1.001788	1.000591	0.999156	0.997503	338.44	339.53	340.69	341.83
<i>PEG-400 + 0.07 mol·kg⁻¹ Glycerol</i>								
0.00000	0.999691	0.998513	0.997109	0.995469				
0.00521	1.000012	0.998829	0.997422	0.995779	338.32	339.65	340.72	341.75
0.01003	1.000307	0.999120	0.997708	0.996063	338.42	339.73	340.84	341.87
0.01511	1.000616	0.999423	0.998009	0.996360	338.53	339.85	340.95	341.98
0.01990	1.000906	0.999708	0.998290	0.996639	338.63	339.95	341.06	342.07
0.02526	1.001227	1.000024	0.998603	0.996949	338.75	340.07	341.18	342.20
0.03009	1.001515	1.000307	0.998882	0.997225	338.85	340.18	341.28	342.31
0.03507	1.001810	1.000597	0.999168	0.997509	338.95	340.29	341.39	342.42
0.04019	1.002111	1.000892	0.999461	0.997798	339.04	340.41	341.48	342.53
<i>PEG-4000 + 0.00 mol·kg⁻¹ Glycerol</i>								
0.00000	0.998211	0.997047	0.995656	0.994039				
0.00534	1.001483	1.000329	0.998950	0.997349	3131.98	3133.05	3134.15	3135.23
0.01070	1.004650	1.003504	1.002139	1.000552	3132.54	3133.73	3134.70	3135.81
0.01604	1.007703	1.006567	1.005214	1.003643	3133.12	3134.26	3135.27	3136.32

0.02134	1.010632	1.009503	1.008164	1.006610	3133.68	3134.90	3135.83	3136.78
0.02662	1.013455	1.012333	1.011007	1.009465	3134.22	3135.48	3136.39	3137.45
0.03124	1.015850	1.014735	1.013417	1.011886	3134.73	3135.96	3136.95	3138.03
0.03737	1.018926	1.017820	1.016518	1.015002	3135.27	3136.51	3137.43	3138.53
0.04260	1.021466	1.020372	1.019074	1.017576	3135.86	3136.98	3138.06	3139.05

PEG-4000 + 0.01 mol·kg⁻¹ Glycerol

0.00000	0.998452	0.997308	0.995869	0.994253				
0.00518	1.001612	1.000478	0.999052	0.997450	3134.36	3135.36	3136.33	3137.74
0.01071	1.004868	1.003743	1.002332	1.000743	3134.71	3135.78	3136.73	3138.14
0.01602	1.007893	1.006776	1.005379	1.003803	3135.07	3136.18	3137.11	3138.54
0.02128	1.010791	1.009682	1.008298	1.006735	3135.43	3136.57	3137.49	3138.92
0.02659	1.013626	1.012524	1.011153	1.009602	3135.78	3136.97	3137.87	3139.32
0.03199	1.016415	1.015319	1.013961	1.012423	3136.13	3137.37	3138.26	3139.71
0.03748	1.019163	1.018074	1.016729	1.015203	3136.49	3137.79	3138.66	3140.12
0.04204	1.021375	1.020291	1.018957	1.017440	3136.81	3138.13	3138.99	3140.46

PEG-4000 + 0.03 mol·kg⁻¹ Glycerol

0.00000	0.998865	0.997707	0.996304	0.994684				
0.00556	1.002239	1.001085	0.999693	0.998085	3135.12	3137.29	3138.84	3140.82
0.01074	1.005281	1.004130	1.002748	1.001150	3135.48	3137.67	3139.20	3141.18
0.01602	1.008278	1.007131	1.005759	1.004172	3135.84	3138.05	3139.57	3141.55

0.02137	1.011213	1.010070	1.008708	1.007131	3136.21	3138.44	3139.95	3141.92
0.02668	1.014038	1.012897	1.011545	1.009978	3136.57	3138.83	3140.32	3142.29
0.03193	1.016741	1.015602	1.014260	1.012703	3136.93	3139.21	3140.69	3142.66
0.03742	1.019481	1.018344	1.017013	1.015465	3137.31	3139.61	3141.07	3143.05
0.04159	1.021503	1.020368	1.019044	1.017504	3137.60	3139.91	3141.36	3143.34
<i>PEG-4000 + 0.05 mol·kg⁻¹ Glycerol</i>								
0.00000	0.999290	0.998124	0.996720	0.995094				
0.00537	1.002532	1.001373	0.999980	0.998365	3137.39	3138.98	3140.47	3142.46
0.01195	1.006360	1.005210	1.003830	1.002228	3137.81	3139.43	3140.91	3142.93
0.01628	1.008794	1.007649	1.006277	1.004684	3138.09	3139.73	3141.20	3143.23
0.02143	1.011606	1.010467	1.009105	1.007521	3138.42	3140.08	3141.54	3143.59
0.02682	1.014453	1.013319	1.011968	1.010394	3138.77	3140.45	3141.90	3143.97
0.03201	1.017113	1.015984	1.014643	1.013077	3139.11	3140.81	3142.25	3144.34
0.03783	1.019999	1.018875	1.017545	1.015988	3139.48	3141.21	3142.63	3144.75
0.04257	1.022274	1.021154	1.019833	1.018284	3139.79	3141.53	3142.95	3145.08
<i>PEG-4000 + 0.07 mol·kg⁻¹ Glycerol</i>								
0.00000	0.999691	0.998513	0.997109	0.995469				
0.00523	1.002842	1.001668	1.000275	0.998647	3138.10	3140.17	3141.56	3143.53
0.01068	1.006018	1.004849	1.003467	1.001850	3138.40	3140.50	3141.88	3143.86
0.01596	1.008993	1.007828	1.006457	1.004850	3138.68	3140.81	3142.20	3144.17

0.02145	1.011987	1.010826	1.009466	1.007870	3138.98	3141.13	3142.52	3144.50
0.02668	1.014744	1.013587	1.012237	1.010651	3139.26	3141.43	3142.83	3144.82
0.03206	1.017497	1.016343	1.015003	1.013427	3139.55	3141.74	3143.15	3145.14
0.03740	1.020138	1.018987	1.017657	1.016090	3139.84	3142.05	3143.46	3145.46
0.04292	1.022789	1.021641	1.020320	1.018763	3140.14	3142.37	3143.79	3145.80

^a m_A is the molality of glycols in aqueous glycerol solutions; Standard uncertainties u are $u_r(m) = 1\%$, $u(T) = 0.01\text{ K}$, $u(\rho) = 0.15\text{ kg}\cdot\text{m}^{-3}$ and $u(p) = 0.01\text{ MPa}$.

Table 4.11

Limiting apparent molar volumes, V_{ϕ}^0 , and experimental slopes, S_V^* of glycols in aqueous solutions of glycerol at different temperatures.

${}^a m_B$	$V_{\phi}^0 \times 10^6 \text{ (m}^3 \cdot \text{mol}^{-1}\text{)}$						$S_V^* \times 10^6 \text{ (m}^3 \cdot \text{kg} \cdot \text{mol}^{-2}\text{)}$					
	$T=293.15 \text{ K}$	$T=298.15 \text{ K}$	$T=303.15 \text{ K}$	$T=308.15 \text{ K}$	$T=293.15 \text{ K}$	$T=298.15 \text{ K}$	$T=303.15 \text{ K}$	$T=308.15 \text{ K}$	$T=293.15 \text{ K}$	$T=298.15 \text{ K}$	$T=303.15 \text{ K}$	$T=308.15 \text{ K}$
PEG-400												
0.00	328.19(±0.03)	329.98(±0.03)	331.49(±0.04)	332.86(±0.02)	134.53(±1.26)	141.54(±1.21)	142.05(±1.53)	151.85(±0.80)				
0.01	330.43(±0.00)	332.15(±0.00)	333.64(±0.00)	335.02(±0.01)	120.14(±0.14)	117.65(±0.12)	115.27(±0.10)	112.74(±0.47)				
0.03	332.84(±0.00)	334.13(±0.01)	335.29(±0.01)	336.40(±0.04)	97.00(±0.19)	94.27(±0.45)	100.13(±0.34)	102.08(±1.46)				
0.05	335.54(±0.01)	336.65(±0.01)	337.86(±0.01)	338.90(±0.01)	70.83(±0.27)	70.12(±0.29)	69.19(±0.33)	71.43(±0.34)				
0.07	338.21(±0.01)	339.52(±0.01)	340.62(±0.01)	341.64(±0.01)	20.86(±0.23)	21.96(±0.28)	21.84(±0.31)	22.20(±0.20)				
PEG-4000												
0.00	3131.44(±0.02)	3132.58(±0.06)	3133.60(±0.04)	3134.68(±0.05)	103.77(±0.86)	105.77(±2.29)	104.64(±1.39)	103.49(±1.97)				
0.01	3134.01(±0.01)	3134.97(±0.00)	3135.96(±0.00)	3137.35(±0.00)	66.32(±0.25)	75.02(±0.12)	72.05(±0.00)	73.79(±0.00)				
0.03	3134.74(±0.00)	3136.88(±0.00)	3138.45(±0.00)	3140.43(±0.00)	68.77(±0.00)	72.85(±0.00)	70.02(±0.00)	69.95(±0.00)				
0.05	3137.04(±0.00)	3138.61(±0.00)	3140.11(±0.00)	3142.09(±0.00)	64.42(±0.00)	68.67(±0.00)	66.75(±0.00)	70.28(±0.00)				
0.07	3137.82(±0.01)	3139.87(±0.01)	3141.25(±0.01)	3143.21(±0.00)	54.04(±0.35)	58.21(±0.22)	59.14(±0.19)	60.20(±0.00)				

${}^a m_B$ is the molality of aqueous solutions of glycerol.

Table 4.12

Partial molar volume of transfer, ΔV_{ϕ}^o of glycols in aqueous solutions of glycerol at different temperatures.

${}^a m_B$ (mol·kg ⁻¹)	$\Delta V_{\phi}^o \times 10^6$ (m ³ ·mol ⁻¹)			
	$T= 293.15$ K	$T= 298.15$ K	$T= 303.15$ K	$T= 308.15$ K
PEG-400				
0.01	2.25	2.17	2.15	2.16
0.03	4.65	4.16	3.80	3.54
0.05	7.35	6.67	6.37	6.05
0.07	10.03	9.54	9.13	8.78
PEG-4000				
0.01	2.57	2.40	2.36	2.68
0.03	3.29	4.31	4.85	5.75
0.05	5.60	6.03	6.51	7.41
0.07	6.38	7.30	7.66	8.54

${}^a m_B$ is the molality of aqueous solutions of glycerol.

Table 4.13

Values of empirical parameters of equation 4.4 for glycols in aqueous glycerol solutions.

${}^a m_B$ (mol·kg ⁻¹)	$A \times 10^6$ (m ³ ·mol ⁻¹)	$B \times 10^6$ (m ³ ·mol ⁻¹ ·K ⁻¹)	$C \times 10^6$ (m ³ ·mol ⁻¹ ·K ⁻²)	R^2	ARD
PEG-400					
0.00	329.96	0.331	-0.0042	0.9999	0.00004
0.01	332.13	0.321	-0.0033	0.9999	0.00003
0.03	334.12	0.246	-0.0018	0.9999	0.00003
0.05	336.69	0.229	-0.0006	0.9999	0.00008
0.07	339.50	0.242	-0.0028	0.9999	0.00004
PEG-4000					
0.00	3132.55	0.217	-0.0005	0.9999	0.00001
0.01	3134.91	0.199	0.0043	0.9999	0.00001
0.03	3136.74	0.381	-0.0017	0.9999	0.00003
0.05	3138.53	0.312	0.0041	0.9999	0.00034
0.07	3139.69	0.356	-0.0009	0.9999	0.00004

^a m_B is the molality of aqueous solutions of glycerol.

Table 4.14

Limiting apparent molar expansibilities, E_{ϕ}^0 for glycols in aqueous glycerol solutions at different temperatures.

${}^a m_B$ (mol·kg ⁻¹)	$E_{\phi}^0 \times 10^6$ (m ³ ·mol ⁻¹ ·K ⁻¹)				$(\partial E_{\phi}^0 / \partial T)_p$ (m ³ ·mol ⁻¹ ·K ⁻²)
	$T= 293.15$ K	$T= 298.15$ K	$T= 303.15$ K	$T= 308.15$ K	
PEG-400					
0.00	0.3736	0.3315	0.2894	0.2473	-0.0084
0.01	0.3545	0.3214	0.2882	0.2551	-0.0066
0.03	0.2636	0.2456	0.2275	0.2095	-0.0036
0.05	0.2356	0.2291	0.2227	0.2163	-0.0013
0.07	0.2702	0.2417	0.2132	0.1848	-0.0057
PEG-4000					
0.00	0.2222	0.2168	0.2115	0.2062	-0.0011
0.01	0.1554	0.1986	0.2418	0.2850	0.0086
0.03	0.3981	0.3812	0.3643	0.3474	-0.0034
0.05	0.2707	0.3120	0.3533	0.3945	0.0083
0.07	0.3649	0.3557	0.3464	0.3371	-0.0019

^a m_B is the molality of aqueous solutions of glycerol.

Table 4.15

Values of ultrasonic speed, c , and apparent molar isentropic compression, $K_{\phi,s}$ of glycols in aqueous solutions of glycerol at different temperatures and experimental pressure, $p = 0.1$ MPa.

${}^a m_A$ (mol·kg ⁻¹)	c (m·s ⁻¹)						$K_{\phi,s} \times 10^6$ (m ³ ·mol ⁻¹ ·GPa ⁻¹)					
	$T=293.15$ K	$T=298.15$ K	$T=303.15$ K	$T=308.15$ K	$T=293.15$ K	$T=298.15$ K	$T=303.15$ K	$T=308.15$ K	$T=293.15$ K	$T=298.15$ K	$T=303.15$ K	$T=308.15$ K
<i>PEG-400 + 0.00 mol·kg⁻¹ Glycerol</i>												
0.00000	1482.25	1495.85	1508.54	1519.14								
0.00498	1483.29	1497.03	1509.60	1520.18	-36.45	-35.70	-35.06	-34.56				
0.01000	1484.35	1498.22	1510.68	1521.23	-41.07	-40.25	-39.54	-38.99				
0.01499	1485.39	1499.40	1511.75	1522.28	-42.60	-41.76	-41.03	-40.47				
0.01992	1486.42	1500.57	1512.80	1523.31	-43.37	-42.52	-41.78	-41.20				
0.02453	1487.39	1501.67	1513.79	1524.27	-43.82	-42.95	-42.21	-41.63				
0.03006	1488.55	1502.98	1514.97	1525.43	-44.18	-43.30	-42.55	-41.97				
0.03525	1489.64	1504.21	1516.08	1526.51	-44.41	-43.54	-42.79	-42.20				
0.03992	1490.62	1505.32	1517.08	1527.49	-44.58	-43.70	-42.94	-42.36				
<i>PEG-400 + 0.01 mol·kg⁻¹ Glycerol</i>												
0.00000	1483.16	1496.96	1509.28	1519.90								
0.00508	1484.22	1498.14	1510.38	1521.02	-36.52	-35.83	-35.22	-34.70				
0.01042	1485.34	1499.38	1511.54	1522.20	-41.13	-40.37	-39.70	-39.13				

0.01501	1486.30	1500.45	1512.53	1523.21	-42.49	-41.70	-41.01	-40.43
0.02069	1487.49	1501.77	1513.76	1524.46	-43.34	-42.54	-41.84	-41.25
0.02547	1488.49	1502.88	1514.79	1525.52	-43.76	-42.96	-42.25	-41.66
0.03014	1489.47	1503.96	1515.80	1526.55	-44.06	-43.24	-42.53	-41.94
0.03512	1490.51	1505.12	1516.88	1527.64	-44.28	-43.47	-42.75	-42.15
0.04056	1491.65	1506.39	1518.06	1528.84	-44.47	-43.65	-42.94	-42.33
<i>PEG-400 + 0.03 mol·kg⁻¹ Glycerol</i>								
0.00000	1483.95	1497.76	1510.03	1520.61				
0.00481	1484.96	1498.87	1511.07	1521.66	-35.98	-35.30	-34.70	-34.19
0.01017	1486.08	1500.11	1512.22	1522.82	-40.99	-40.22	-39.56	-39.00
0.01521	1487.13	1501.28	1513.31	1523.92	-42.48	-41.70	-41.01	-40.43
0.02019	1488.17	1502.43	1514.38	1525.00	-43.24	-42.44	-41.74	-41.16
0.02530	1489.24	1503.61	1515.49	1526.11	-43.70	-42.90	-42.20	-41.61
0.02990	1490.20	1504.68	1516.48	1527.11	-43.99	-43.18	-42.48	-41.88
0.03506	1491.28	1505.87	1517.59	1528.23	-44.23	-43.42	-42.71	-42.11
0.03928	1492.17	1506.85	1518.50	1529.15	-44.38	-43.57	-42.85	-42.26
<i>PEG-400 + 0.05 mol·kg⁻¹ Glycerol</i>								
0.00000	1484.77	1498.57	1510.70	1521.24				
0.00518	1485.86	1499.76	1511.82	1522.38	-36.63	-35.93	-35.33	-34.82
0.01004	1486.88	1500.88	1512.87	1523.44	-40.88	-40.12	-39.47	-38.91
0.01489	1487.90	1501.99	1513.92	1524.51	-42.37	-41.59	-40.91	-40.34

0.01992	1488.95	1503.15	1515.01	1525.61	-43.16	-42.36	-41.67	-41.09
0.02505	1490.03	1504.33	1516.12	1526.73	-43.64	-42.83	-42.14	-41.55
0.02994	1491.06	1505.45	1517.17	1527.81	-43.95	-43.14	-42.44	-41.85
0.03489	1492.10	1506.59	1518.24	1528.89	-44.17	-43.36	-42.66	-42.07
0.04101	1493.38	1508.00	1519.57	1530.23	-44.38	-43.57	-42.87	-42.27

PEG-400 + 0.07 mol·kg⁻¹ Glycerol

0.00000	1485.48	1499.35	1511.43	1521.82				
0.00521	1486.58	1500.54	1512.56	1522.93	-36.65	-35.95	-35.36	-34.85
0.01003	1487.59	1501.64	1513.60	1523.96	-40.84	-40.08	-39.43	-38.88
0.01511	1488.66	1502.80	1514.70	1525.05	-42.38	-41.59	-40.92	-40.35
0.01990	1489.67	1503.89	1515.73	1526.07	-43.11	-42.31	-41.63	-41.06
0.02526	1490.79	1505.11	1516.89	1527.22	-43.61	-42.80	-42.12	-41.54
0.03009	1491.81	1506.22	1517.94	1528.25	-43.91	-43.10	-42.41	-41.82
0.03507	1492.86	1507.35	1519.01	1529.32	-44.14	-43.32	-42.63	-42.04
0.04019	1493.93	1508.52	1520.12	1530.41	-44.32	-43.50	-42.80	-42.21

PEG-4000 + 0.00 mol·kg⁻¹ Glycerol

0.00000	1482.25	1495.85	1508.54	1519.14				
0.00534	1492.16	1505.52	1518.43	1529.06	-37.35	-36.59	-35.94	-35.43
0.01070	1502.09	1515.48	1528.33	1539.01	-41.77	-40.94	-40.23	-39.67
0.01604	1512.00	1525.41	1538.22	1548.93	-43.33	-42.47	-41.74	-41.17
0.02134	1521.83	1535.26	1548.02	1558.78	-44.17	-43.30	-42.55	-41.98

0.02662	1531.63	1545.08	1557.79	1568.58	-44.72	-43.84	-43.09	-42.51
0.03124	1540.19	1553.66	1566.34	1577.16	-45.08	-44.20	-43.44	-42.85
0.03737	1551.55	1565.04	1577.66	1588.53	-45.46	-44.57	-43.80	-43.22
0.04260	1561.26	1574.78	1587.35	1598.26	-45.72	-44.83	-44.06	-43.47
<i>PEG-4000 + 0.01 mol·kg⁻¹ Glycerol</i>								
0.00000	1483.16	1496.96	1509.28	1519.90				
0.00518	1492.79	1506.56	1518.88	1529.53	-36.97	-36.28	-35.66	-35.14
0.01071	1503.05	1516.80	1529.11	1539.79	-41.66	-40.88	-40.21	-39.64
0.01602	1512.92	1526.64	1538.95	1549.66	-43.20	-42.41	-41.71	-41.12
0.02128	1522.68	1536.38	1548.68	1559.42	-44.04	-43.23	-42.52	-41.92
0.02659	1532.55	1546.22	1558.52	1569.29	-44.59	-43.77	-43.06	-42.46
0.03199	1542.57	1556.22	1568.51	1579.31	-45.01	-44.18	-43.46	-42.86
0.03748	1552.78	1566.40	1578.69	1589.52	-45.34	-44.51	-43.78	-43.18
0.04204	1561.24	1574.83	1587.12	1597.98	-45.57	-44.73	-44.01	-43.40
<i>PEG-4000 + 0.03 mol·kg⁻¹ Glycerol</i>								
0.00000	1483.95	1497.76	1510.03	1520.61				
0.00556	1494.27	1508.07	1520.30	1530.93	-37.54	-36.83	-36.21	-35.69
0.01074	1503.90	1517.69	1529.89	1540.56	-41.63	-40.86	-40.18	-39.62
0.01602	1513.70	1527.49	1539.65	1550.36	-43.16	-42.36	-41.67	-41.09
0.02137	1523.63	1537.41	1549.53	1560.29	-44.00	-43.19	-42.49	-41.89
0.02668	1533.49	1547.26	1559.35	1570.15	-44.55	-43.73	-43.02	-42.42

0.03193	1543.24	1557.00	1569.05	1579.90	-44.95	-44.12	-43.41	-42.81
0.03742	1553.44	1567.20	1579.20	1590.10	-45.28	-44.45	-43.73	-43.13
0.04159	1561.19	1574.93	1586.92	1597.85	-45.49	-44.66	-43.94	-43.33
<i>PEG-4000 + 0.05 mol·kg⁻¹ Glycerol</i>								
0.00000	1484.77	1498.57	1510.70	1521.24				
0.00537	1494.73	1508.54	1520.63	1531.20	-37.21	-36.51	-35.90	-35.38
0.01195	1506.95	1520.78	1532.81	1543.42	-42.04	-41.26	-40.59	-40.02
0.01628	1514.99	1528.83	1540.82	1551.46	-43.16	-42.37	-41.68	-41.10
0.02143	1524.55	1538.41	1550.35	1561.02	-43.96	-43.15	-42.45	-41.87
0.02682	1534.55	1548.42	1560.31	1571.02	-44.51	-43.69	-42.99	-42.40
0.03201	1544.19	1558.07	1569.92	1580.66	-44.90	-44.08	-43.37	-42.77
0.03783	1555.00	1568.90	1580.70	1591.47	-45.25	-44.42	-43.71	-43.11
0.04257	1563.80	1577.70	1589.46	1600.27	-45.48	-44.65	-43.94	-43.33
<i>PEG-4000 + 0.07 mol·kg⁻¹ Glycerol</i>								
0.00000	1485.48	1499.35	1511.43	1521.82				
0.00523	1495.19	1509.07	1521.11	1531.53	-36.95	-36.25	-35.65	-35.14
0.01068	1505.31	1519.20	1531.20	1541.65	-41.52	-40.75	-40.09	-39.53
0.01596	1515.12	1529.02	1540.98	1551.46	-43.06	-42.26	-41.58	-41.01
0.02145	1525.32	1539.24	1551.15	1561.66	-43.92	-43.11	-42.42	-41.84
0.02668	1535.03	1548.96	1560.83	1571.37	-44.45	-43.63	-42.94	-42.35
0.03206	1545.04	1558.97	1570.81	1581.38	-44.86	-44.03	-43.33	-42.74

0.03740	1554.94	1568.89	1580.68	1591.28	-45.18	-44.35	-43.64	-43.05
0.04292	1565.20	1579.16	1590.91	1601.54	-45.46	-44.62	-43.91	-43.31

^a m_A is the molality of glycols in aqueous glycerol solutions; Standard uncertainties u are $u_r(m) = 1\%$, $u(T) = 0.01$ K, $u(c) = 0.5$ m·s⁻¹ and $u(p) = 0.01$ MPa.

Table 4.16

Limiting apparent molar isentropic compression, $K_{\phi,s}^0$ and experimental slope, S_K^* for glycols in aqueous solutions of glycerol at different temperatures.

${}^a m_B$ (mol·kg ⁻¹)	$K_{\phi,s}^0 \times 10^6$ (m ³ ·mol ⁻¹ ·GPa ⁻¹)			$S_K^* \times 10^6$ (kg·m ³ ·mol ⁻² ·GPa ⁻¹)			
	$T=293.15$ K	$T=298.15$ K	$T=303.15$ K	$T=293.15$ K	$T=298.15$ K	$T=303.15$ K	$T=308.15$ K
PEG-400							
0.00	-38.36(±1.24)	-37.59(±1.22)	-36.92(±1.20)	-186.88(±48.97)	-183.84(±48.20)	-181.21(±47.53)	-179.21(±47.02)
0.01	-38.35(±1.21)	-37.64(±1.19)	-37.00(±1.18)	-182.00(±47.41)	-179.01(±46.65)	-176.56(±46.02)	-174.63(±45.53)
0.03	-37.98(±1.30)	-37.27(±1.28)	-36.65(±1.26)	-195.23(±51.54)	-192.05(±50.71)	-189.42(±50.03)	-187.37(±49.50)
0.05	-38.40(±1.16)	-37.68(±1.14)	-37.06(±1.13)	-176.82(±45.75)	-173.95(±45.01)	-171.61(±44.42)	-169.76(±43.95)
0.07	-38.33(±1.15)	-37.61(±1.13)	-36.99(±1.11)	-178.55(±45.27)	-175.63(±44.54)	-173.28(±43.96)	-171.46(±43.50)
PEG-4000							
0.00	-39.00(±1.16)	-38.21(±1.14)	-37.54(±1.12)	-185.99(±43.18)	-183.11(±42.51)	-180.56(±41.90)	-178.71(±41.45)
0.01	-38.74(±1.20)	-38.01(±1.18)	-37.37(±1.17)	-190.72(±44.84)	-187.69(±44.12)	-185.25(±43.53)	-183.33(±43.06)
0.03	-38.96(±1.08)	-38.23(±1.05)	-37.59(±1.05)	-182.65(±40.49)	-179.71(±39.84)	-177.35(±39.30)	-175.51(±38.88)
0.05	-38.91(±1.18)	-38.18(±1.15)	-37.55(±1.15)	-181.60(±43.58)	-178.71(±42.88)	-176.40(±42.31)	-174.57(±41.86)
0.07	-38.71(±1.18)	-37.98(±1.15)	-37.35(±1.15)	-185.84(±43.81)	-182.85(±43.11)	-180.50(±42.54)	-178.68(±42.10)

${}^a m_B$ is the molality of aqueous solutions of glycerol.

Table 4.17

Partial molar isentropic compression of transfer, $\Delta K_{\phi,s}^o$ of glycols in aqueous solutions of glycerol at different temperatures.

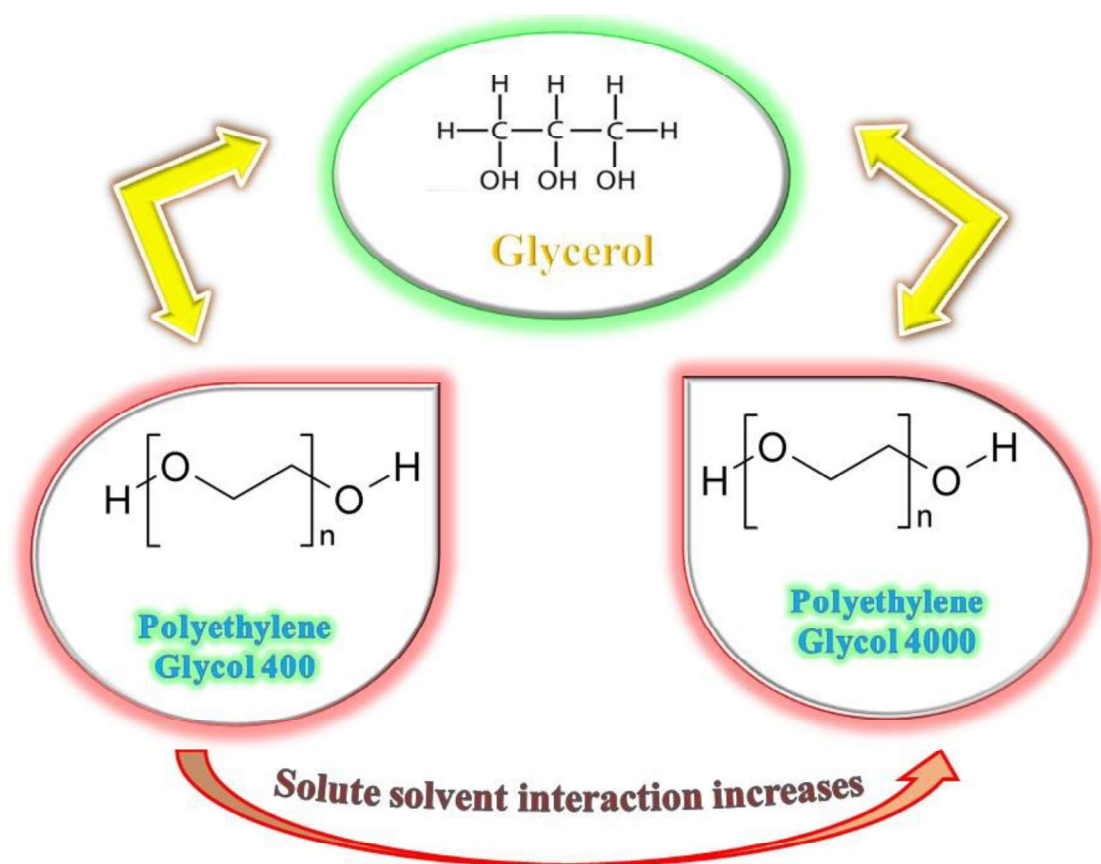
${}^a m_B$ (mol·kg ⁻¹)	$\Delta K_{\phi,s}^o \times 10^6$ (m ³ ·mol ⁻¹ ·GPa ⁻¹)			
	$T= 293.15$ K	$T= 298.15$ K	$T= 303.15$ K	$T= 308.15$ K
PEG-400				
0.01	0.01	-0.05	-0.09	-0.07
0.03	0.38	0.32	0.27	0.28
0.05	-0.04	-0.09	-0.14	-0.12
0.07	0.03	-0.03	-0.08	-0.07
PEG-4000				
0.01	0.27	0.20	0.17	0.18
0.03	0.05	-0.01	-0.05	-0.04
0.05	0.10	0.04	-0.01	0.01
0.07	0.30	0.24	0.19	0.19

${}^a m_B$ is the molality of aqueous solutions of glycerol.

Table 4.18

Pair and triplet interaction coefficients of glycols in aqueous solutions of glycerol at different temperatures.

T (K)	$V_{AB} \times 10^6$ ($\text{m}^3 \cdot \text{mol}^{-2} \cdot \text{kg}$)	$V_{ABB} \times 10^6$ ($\text{m}^3 \cdot \text{mol}^{-3} \cdot \text{kg}^2$)	$K_{AB} \times 10^6$ ($\text{m}^3 \cdot \text{mol}^{-2} \cdot \text{kg} \cdot \text{GPa}^{-1}$)	$K_{ABB} \times 10^6$ ($\text{m}^3 \cdot \text{mol}^{-3} \cdot \text{kg}^2 \cdot \text{GPa}^{-1}$)
PEG-400				
293.15	86.42	-147.95	5.55	-54.78
298.15	74.75	-72.36	3.89	-42.27
303.15	69.08	-45.42	2.82	-35.17
308.15	64.63	-27.50	3.27	-39.03
PEG-4000				
293.15	79.83	-329.47	1.58	2.26
298.15	91.46	-383.74	-0.07	14.24
303.15	101.97	-458.34	-1.03	20.19
308.15	121.14	-582.98	-0.53	15.62



Scheme 1: PEGs and glycerol interactions

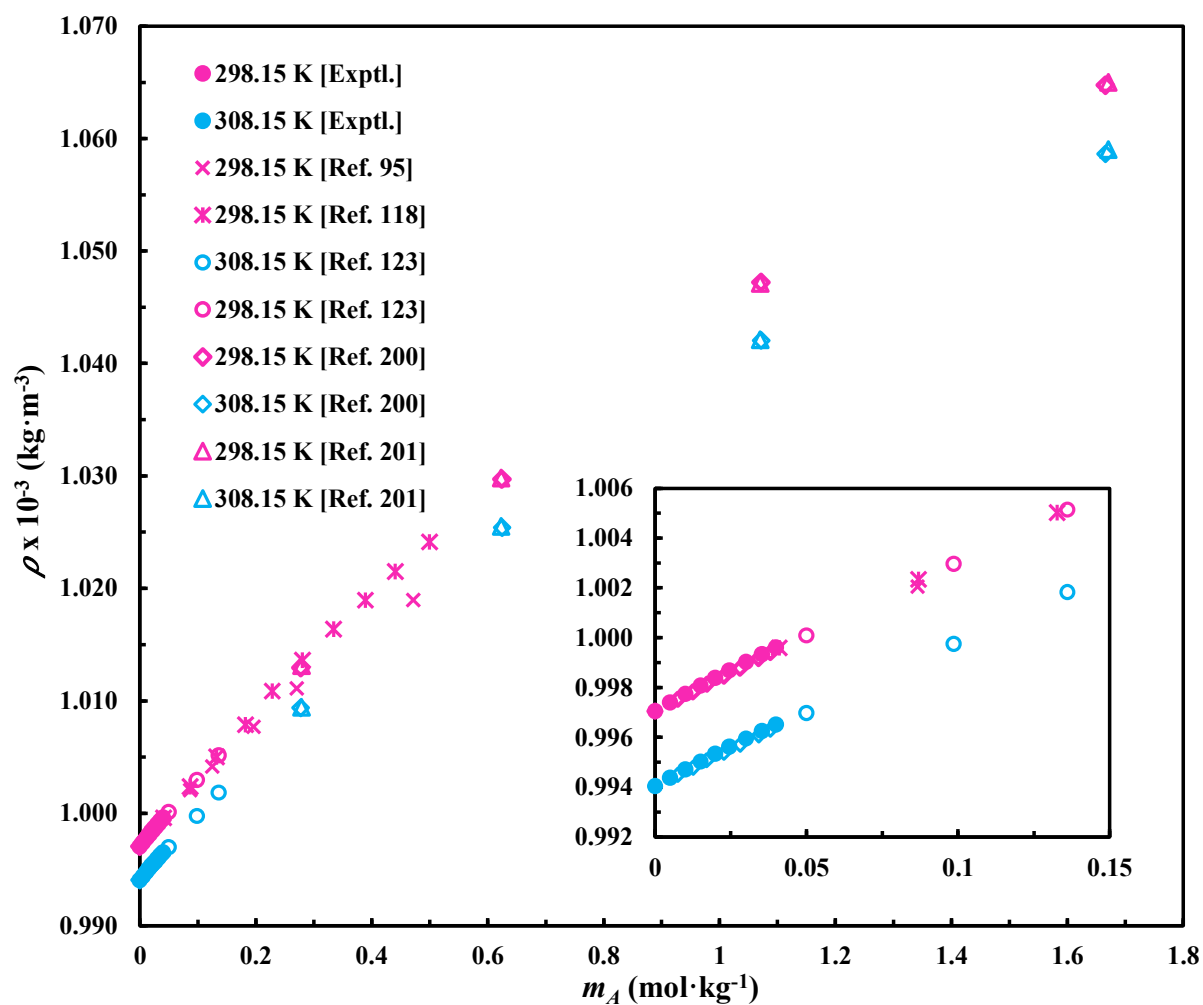


Figure 4.12: Plots of experimental and literature values [95, 118, 123, 200, 201] of densities for (PEG-400 + water) mixtures at different temperatures.

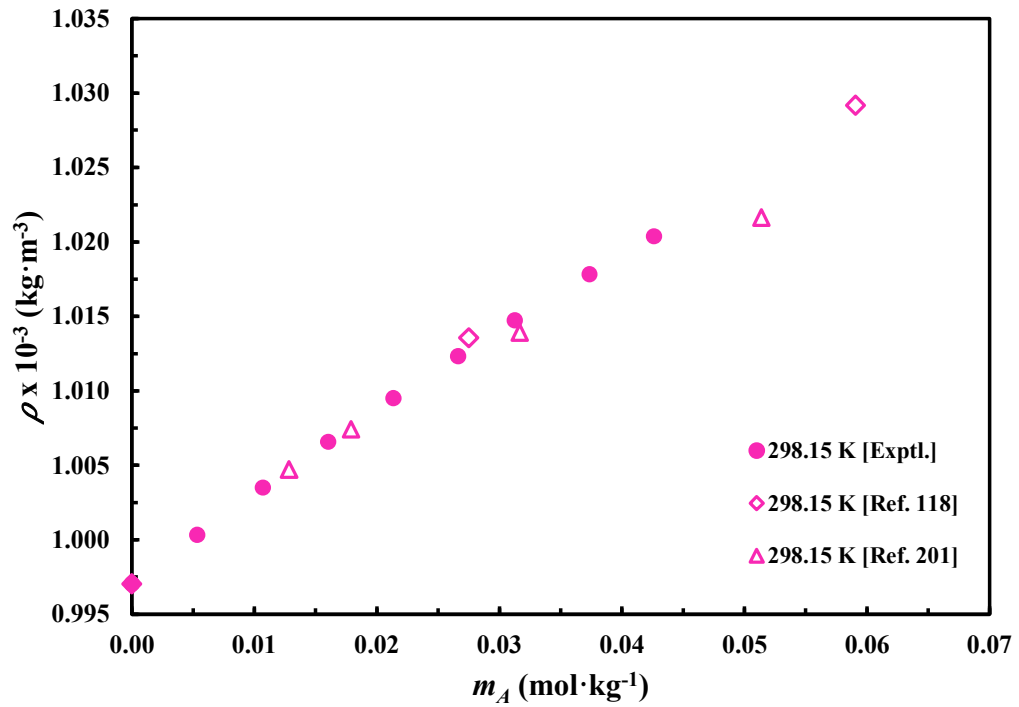


Figure 4.13: Plots of experimental and literature values [118, 201] of densities for (PEG-4000 + water) mixtures at temperature 298.15 K.

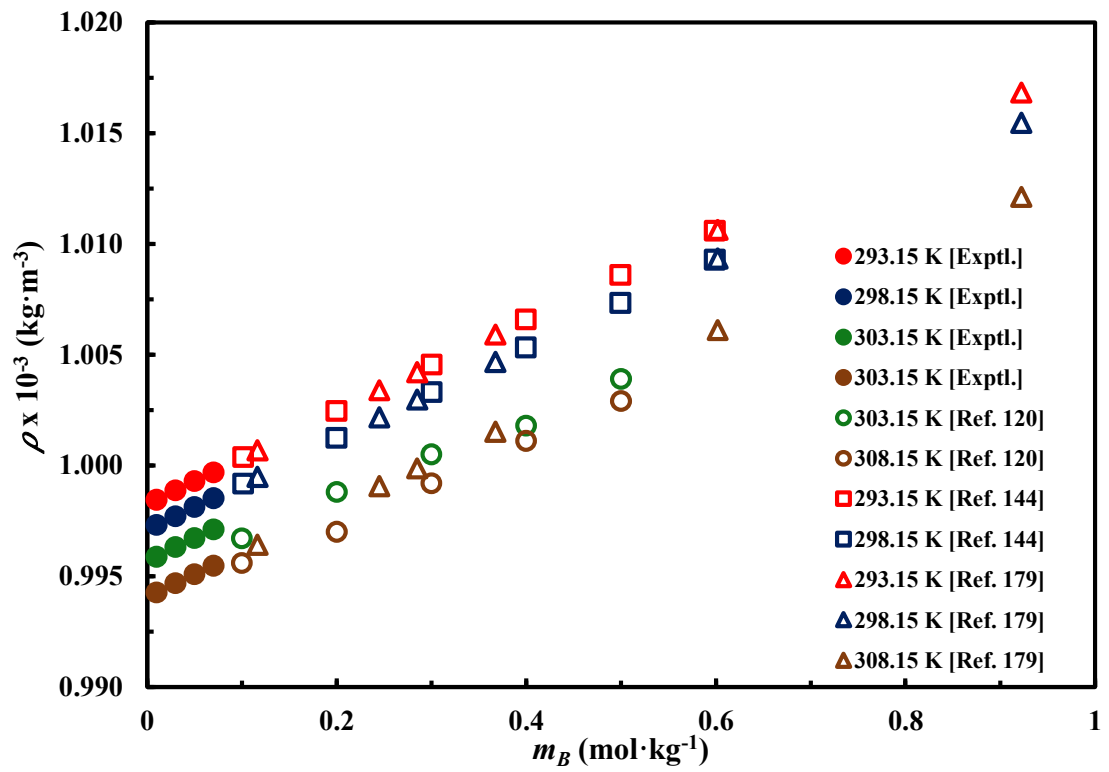


Figure 4.14: Plots of experimental and literature values [120, 144, 179] of densities for (glycerol + water) mixtures at 298.15 K.

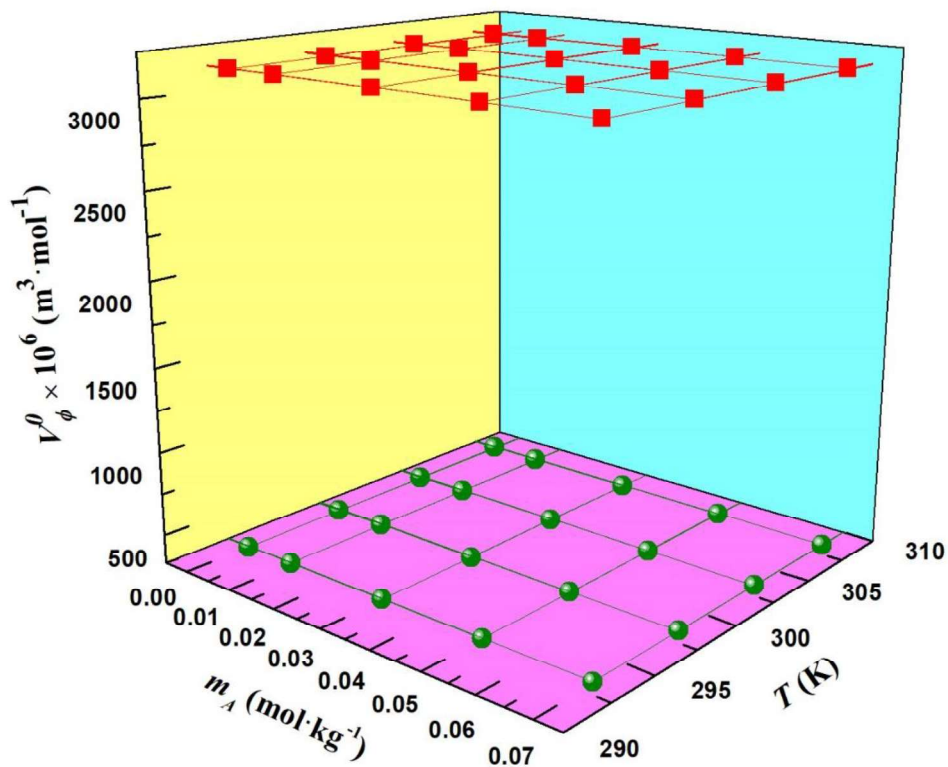


Figure 4.15: Plots of partial molar volume V_ϕ^0 for PEG-400 (●) and PEG-4000 (■) in different concentrations of aqueous glycerol solutions at different temperatures.

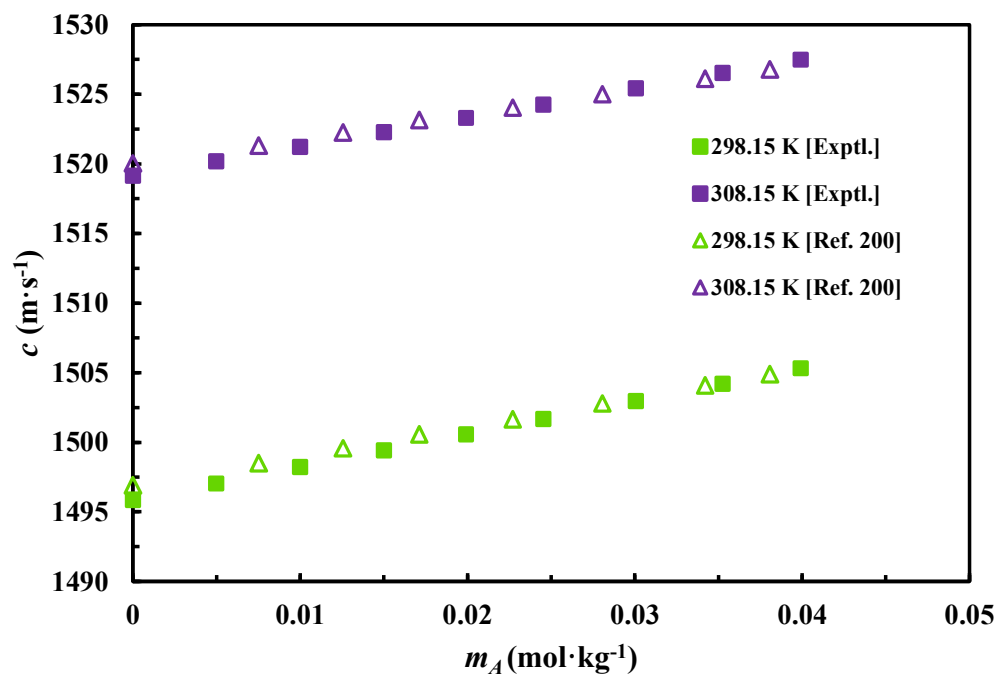


Figure 4.16: Plots of experimental and literature values [200] of ultrasonic speeds for (PEG-400 + water) mixtures at temperatures 298.15 K and 308.15 K.

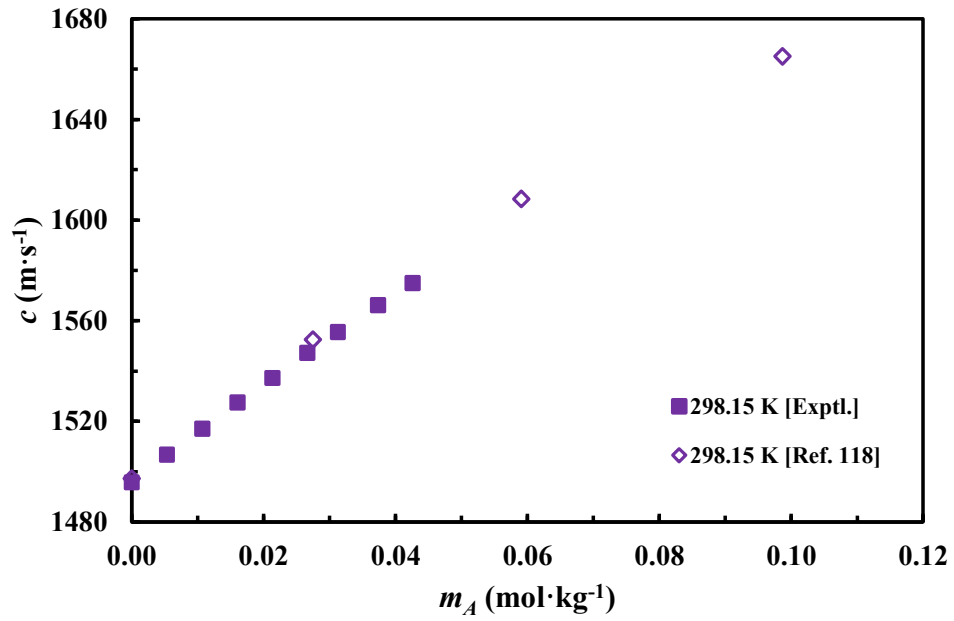


Figure 4.17: Plots of experimental and literature values [118] of ultrasonic speeds for (PEG-4000 + water) mixtures at temperature 298.15 K.

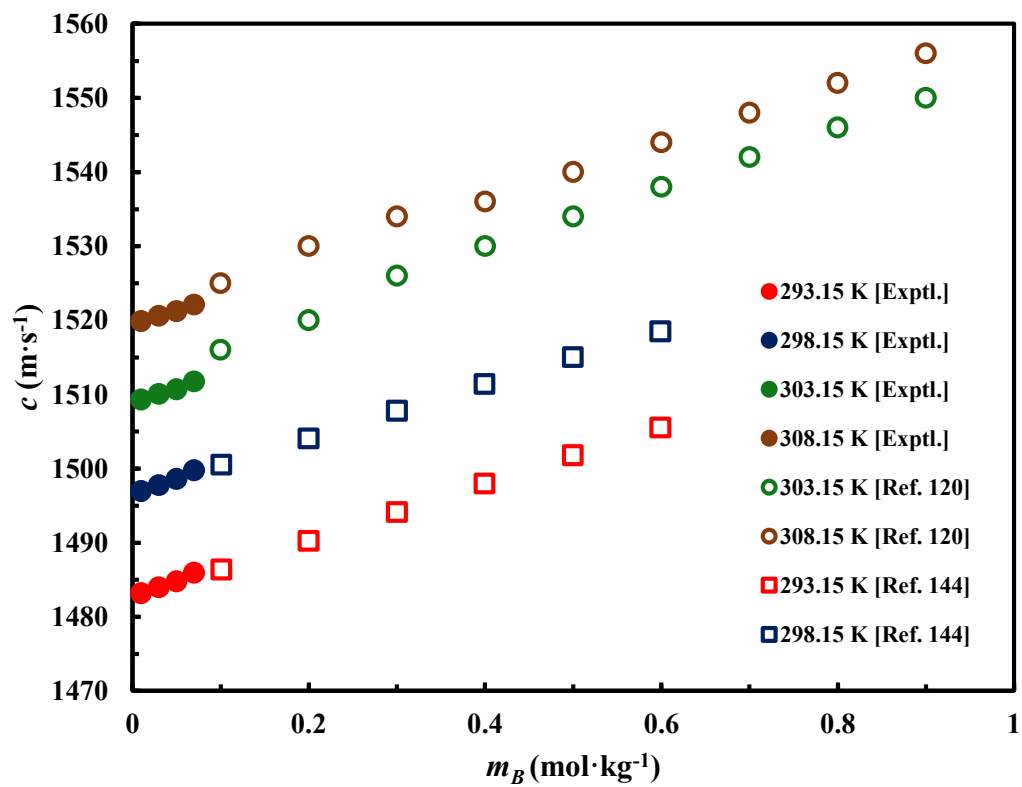


Figure 4.18: Plots of experimental and literature values [120, 144] of ultrasonic speeds for (glycerol + water) mixtures at 298.15 K.

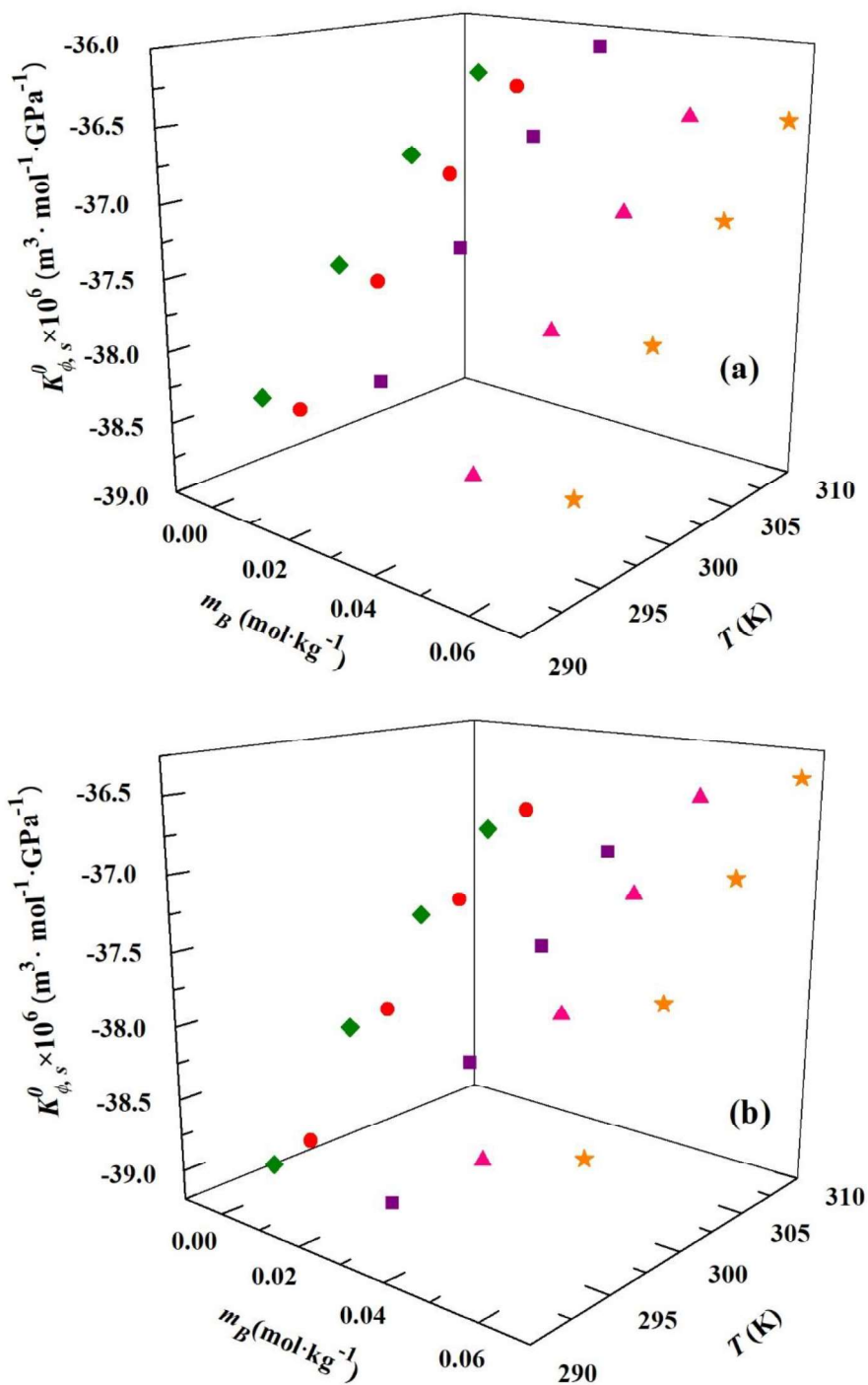


Figure 4.19: Plots of variation of partial molar isentropic compression, $K_{\phi,s}^0$ for polyethylene glycols (a) PEG-400 (b) PEG-4000 at different temperatures and concentrations of aqueous glycerol solutions (\blacklozenge , $0.00 \text{ mol} \cdot \text{kg}^{-1}$; \bullet , $0.01 \text{ mol} \cdot \text{kg}^{-1}$; \blacksquare , $0.03 \text{ mol} \cdot \text{kg}^{-1}$; \blacktriangle , $0.05 \text{ mol} \cdot \text{kg}^{-1}$; \star , $0.07 \text{ mol} \cdot \text{kg}^{-1}$].

Section III

In previous sections we have reported the densities and ultrasonic speeds of three ethylene glycols (EG, DEG and TEG) and two polyethylene glycols (PEG-400 and PEG-4000) with glycerol. In continuation to our work on sugar alcohols with glycols, in the present section we have studied EG, DEG and TEG in aqueous sorbitol solutions.

Density

The experimental values of densities, ρ of solutions for EG, DEG and TEG in (0.00, 0.01, 0.03, 0.05) mol·kg⁻¹ aqueous solutions of sorbitol were measured at temperatures $T = (288.15, 298.15, 308.15, 318.15)$ K. The density values for all the liquid mixtures at different temperatures are attributed in Table 4.19. It is observed from Table 4.19 that at a particular concentration of sorbitol, the density values of the liquid mixtures are increasing with rise in concentration of glycol and decreasing with rise in temperature. The plots of experimental data and literature data [182-188, 202, 204-206] of densities of (EG, DEG, TEG) + water are shown in Figure 4.20-4.22 and the plots of experimental and literature values [189, 193, 194] for density and ultrasonic velocity of sorbitol + water are shown in Figure 4.23 and 4.24 respectively. It is noted from the figures that the experimental values follow the same trend as of literature values.

Apparent molar volume

The experimental density values are used to calculate apparent molar volumes (V_ϕ) from equation 4.1. In Table 4.19, the computed values of apparent molar volume are incorporated. The data given in Table 4.19 discloses that at a particular concentration of sorbitol, the values of apparent molar volume are found to be increasing with increase in molality of glycols and temperature. Surge in the values of V_ϕ with upsurge in concentration of sorbitol is also observed from Table 4.19, which infers that the solute-solvent interactions are significantly enhanced. The rise in V_ϕ values is also detected with respect to molar mass of glycols, i.e. with the increase in molar mass of glycols the values of apparent molar volume also increase at all temperatures and for all concentrations of sorbitol resulting in maximum solute-solvent interactions in case of TEG mixtures as compared to EG and DEG as shown in Scheme 2.

Partial molar volume

The partial molar volume V_{ϕ}^0 is calculated from equation 4.2, by the means of least squares fitting of apparent molar volume V_{ϕ} . The values of V_{ϕ}^0 and S_V^* along with standard errors computed from V_{ϕ} values by least squares fitting of it to equation 4.2 are collected in Table 4.20. The whole V_{ϕ}^0 values are positive and are rising with rise in temperature and concentration of sorbitol in all three glycols as represented in Figure 4.25. From the statistic that OH bending vibrational band shifts towards a higher frequency in EGs-water mixtures suggests that there are possible hydrogen bonding interactions of hydrogen atoms in water with hydroxyl oxygen atoms in glycols by cross-linking in the form of ...HOH... [119]. Further, with increasing molar mass of glycols, the V_{ϕ}^0 values also increase at each temperature resultant of which is greatest V_{ϕ}^0 values in case of TEG which indicates predominance of the solute-solvent interactions in TEG as compared to DEG and EG. By the definition, the V_{ϕ}^0 values are independent of solute-solute interaction, hence provides information concerning solute-solvent interactions [202]. As per co-sphere overlap model [204, 205], there is increase in volume due to an overlap of hydration co-spheres of two ionic species while an overlap of ion-hydrophobic groups and hydrophobic-hydrophobic groups results in decreased volume. It is inferred that ion-hydrophilic interactions are more dominating over hydrophobic-hydrophobic and ion-hydrophobic interactions, as specified by positive V_{ϕ}^0 values. The escalation in V_{ϕ}^0 values for glycols with increasing concentration of sorbitol and temperature can be elucidated as the release of few solvation molecules from loose solvation layers of solutes into the solution. At higher temperature, the expansion of solution occurs, due to the fact that the solvent from secondary solvation layers of the solute is released into the bulk of solvent, as deduced from greater V_{ϕ}^0 values at higher temperatures. The reasons for change in partial molar volume can be attributed to the weakening of H-bond, thermal expansion, release of molecules from solvation layer etc. The values of V_{ϕ}^0 increase with increase in glycol concentration because of strong attractive interactions between hydroxyl groups of EGs and sorbitol. Further the magnitude of S_V^* values is found to be positive for all the sample mixtures. Small values of S_V^* in comparison to V_{ϕ}^0 indicates that solute-solvent interactions are predominant over solute-

solute interactions. It is indicative from irregular trend of S_V^* that solute-solute interactions are influenced by other factors also [182].

Partial molar volume of transfer

At infinite dilution, the transfer volume of glycols from water to aqueous sorbitol solutions is calculated from equation 4.3. The computed values of ΔV_ϕ^0 are listed in Table 4.21. For all EGs, ΔV_ϕ^0 values are positive and are escalating with rise in concentration of sorbitol which infers huge desiccation effect on glycols. With respect to increasing temperature, no regular trend is observed in ΔV_ϕ^0 values. Concerning the structure of pure water, the existence of a structural network of water with relatively large empty areas – clathrates that can be penetrated by different molecules, is assumed by the models described by Pauling [183, 184]. Probably very small amounts of EGs can be placed in the cages of the water structures so as not to abolish the cage structure. Rather higher content of glycol destroys a cage structure and because of possibility of hydrogen bond formation between organic molecules and water, new structures are created [170]. According to co-sphere overlap model [204, 205] regarding ΔV_ϕ^0 values, there is insignificant contribution from solute-solute interactions and hence provide considerable information about solute-solvent interactions. Hydrophobic–hydrophobic interactions, ion–hydrophobic interactions, hydrophilic–hydrophilic interactions, ion–hydrophilic interactions are the various possible interactions which may occur between EG / DEG / TEG and sorbitol molecules. In accordance with co-sphere overlap model, hydrophobic–hydrophobic interactions and ion–hydrophobic interactions make negative contribution to the ΔV_ϕ^0 values while a positive contribution is made by ion–hydrophilic interactions and hydrophilic–hydrophilic interactions. Hence, it can be inferred that hydrophilic–hydrophilic interactions and ion–hydrophilic interactions are dominant over other interactions in EGs + water + sorbitol solutions.

Temperature dependent partial molar volume

With the use of general polynomial equation, equation 4.4, the variation of apparent molar volumes (V_ϕ^0) with the temperature at infinite dilution can be expressed. In aqueous

sorbitol, the value of these constants for EG, DEG and TEG are given in Table 4.22. A barely statistically significant coefficient, C has negative values for DEG and both positive and negative values for EG and TEG in aqueous sorbitol solutions. These parameters were used to calculate V_{ϕ}^0 and deviations attained from calculated and experimental values are also indexed in Table 4.22. The deviations are calculated from equation 4.5. The values listed in Table 4.22 for deviations are very small which fits into the polynomial equation very finely which is evident from R^2 values in the present study.

To calculate partial molar expansibilities, equation 4.6 is used. At infinite dilution, the temperature dependence of partial molar volume (V_{ϕ}^0) can be represented in terms of absolute temperature (T) by the same equation 4.6. The limiting apparent molar expansibility at infinite dilution, $E_{\phi}^0 = (\partial V_{\phi}^0 / \partial T)_p$ is considered to be a beneficial measure [185] of solute-solvent interaction existing in the solution. To determine the capacity of solute as a structure breaker or structure maker in the mixed solvent system, the general thermodynamic expression provided as equation 4.7 in supporting information, developed by Hepler [186] is used. The tendency of a dissolved solute as a structure breaker or structure maker in a solvent is determined [187, 206] by the sign of $(\partial E_{\phi}^0 / \partial T)_p$ which recommends that positive and very small negative values of $(\partial E_{\phi}^0 / \partial T)_p$ are noticed for structure making solutes while negative values of $(\partial E_{\phi}^0 / \partial T)_p$ are observed for solutes having structure breaking capacity. The data of partial molar expansibilities E_{ϕ}^0 and $(\partial E_{\phi}^0 / \partial T)_p$ are attributed in Table 4.23. The limiting apparent molar expansibilities are positive at all temperatures and concentrations of sorbitol. The positive E_{ϕ}^0 values indicate that the solute-solvent interactions are present in these systems, as already suggested by apparent molar volume data. No regular trend is observed for the values of E_{ϕ}^0 with an increase in the temperature as well as in the concentration of sorbitol solutions. The positive and small negative $(\partial E_{\phi}^0 / \partial T)_p$ values for the mixtures of glycols suggests the structure making capability of glycols in all aqueous sorbitol solutions.

Ultrasonic speeds

The measured values of ultrasonic speed, c of EG, DEG and TEG in (0.00, 0.01, 0.03, 0.05) mol·kg⁻¹ aqueous solutions of sorbitol are obtained at temperatures $T = (288.15, 298.15,$

308.15, 318.15) K. The values of ultrasonic speed of all the liquid mixtures at different temperatures are provided in Table 4.24. It is observed from Table 4.24 that the values of speed of sound vary in sequence with respect to temperature as well as concentration of sorbitol. Moreover, the ultrasonic speeds rise with rise in molality of glycols for a particular concentration of sorbitol.

Apparent molar isentropic compression

With the use of equation 4.8, the apparent molar isentropic compression for glycols in aqueous and mixed aqueous solutions of sorbitol at different temperatures, is determined. Isentropic compressibility is computed from the relation given by equation 4.9. The computed values of $K_{\phi,s}$ for various molal concentrations (m_A) of EG, DEG and TEG in (0.00, 0.01, 0.03 and 0.05) mol·kg⁻¹ sorbitol at different temperatures are collected in Table 4.24. From the calculated $K_{\phi,s}$ values, it is scrutinized that the values are negative at all concentrations of sorbitol and at all temperatures. These values of $K_{\phi,s}$ become less negative with increase in temperature and concentration of sorbitol but with the increase in molality of glycols the $K_{\phi,s}$ values become more negative. The negative $K_{\phi,s}$ values indicate that the water molecules around solute are less compressible than the water molecules in the bulk solution [206] resulting in the tightening of the water molecules around it because of hydrophobic interactions of a non-polar group. Therefore, the pressure on bulk water molecules results in compressibility of the solution, which further suggests the strong solute-solvent interactions between the molecules of EGs and the molecules of sorbitol.

Partial molar isentropic compression

The partial molar isentropic compression ($K_{\phi,s}^o$) can be calculated from the variation of apparent molar isentropic compression ($K_{\phi,s}$) with molal concentration of EGs by equation 4.10. The $K_{\phi,s}^o$ values and S_K^* values altogether with standard errors derived by the method of least squares fitting are indexed in Table 4.25. The solute-solute interactions are found to be negligible at infinite dilution since the S_K^* values are small in size which further suggests that solute-solvent interactions [188] are dominant in the present liquid mixtures.

The values of $K_{\phi,s}^o$ are found to be negative and become less negative with the increase in temperature which means that some water molecules are released to bulk. These negative $K_{\phi,s}^o$ values are increased also with increasing concentration of sorbitol. The larger negative values of $K_{\phi,s}^o$ for glycols at low temperature are attributed to the strong attractive interactions between glycols and water [189]. Further, the attractive interactions between sorbitol and water molecules induces dehydration of glycol, due to which at higher concentrations of sorbitol, the water molecules around the glycols are more compressible than those at lower sorbitol concentrations.

Partial molar isentropic compressions of transfer

For each glycol from water to aqueous sorbitol solutions at infinite dilution, the partial molar isentropic compressions of transfer ($\Delta K_{\phi,s}^o$) were calculated using equation 4.11. The computed values of $\Delta K_{\phi,s}^o$ are indexed in Table 4.26. All the values of $\Delta K_{\phi,s}^o$ are found to be positive at all temperatures and all concentrations of sorbitol. From the table, it is deduced that with increasing concentration of sorbitol, $\Delta K_{\phi,s}^o$ values also increase. The positive $\Delta K_{\phi,s}^o$ values infer the structure making tendency of ions and dominance of interactions between glycols and sorbitol. With increasing concentration of sorbitol, the interaction between glycols and sorbitol intensifies.

Pair and triplet interaction coefficients

The interaction coefficients are calculated based upon McMillan-Mayer [193] theory of solutions which permits the separation of effects due to interactions between the pairs of solute molecules as well as those due to its interactions between more than two molecules. This theory was further discussed by Friedman and Krishnan [194] and Franks [195] so that solute-cosolute interactions can be included in the solvation spheres. So, limiting apparent molar volume of transfer and limiting apparent molar isentropic compression of transfer can be expressed as equations 4.12 and 4.13. The pair and triplet coefficients are denoted by the corresponding parameters V_{AB} , V_{ABB} for volume and K_{AB} , K_{ABB} for isentropic compression. The values of constants (V_{AB} , V_{ABB} , K_{AB} and K_{ABB}) and are stated in Table 4.27. For all glycols, the pair interaction coefficients V_{AB} are positive except for

EG at 318.15 K while triplet interaction coefficient V_{ABB} is negative at all temperatures except for EG. The pair interaction coefficient K_{AB} is positive for all glycols at all temperatures but the triplet interaction coefficient K_{ABB} is found to be negative at all temperatures except for positive K_{ABB} at 288.15 K. The overall positive values of pair interaction coefficients for volumetric and compressibility measurements (V_{AB} and K_{AB}) predict [196] that pair wise interactions are dominating in glycol-sorbitol-water mixtures.

Table 4.19

Values of densities, ρ , and apparent molar volumes, V_ϕ of glycols in aqueous solutions of sorbitol at different temperatures and experimental pressure, $p = 0.1$ MPa.

$^a m_A$ (mol·kg ⁻¹)	$\rho \times 10^{-3}$ (kg·m ⁻³)				$V_\phi \times 10^6$ (m ³ ·mol ⁻¹)			
	$T = 288.15$ K	$T = 298.15$ K	$T = 308.15$ K	$T = 318.15$ K	$T = 288.15$ K	$T = 298.15$ K	$T = 308.15$ K	$T = 318.15$ K
<i>EG + 0.00 mol·kg⁻¹ Sorbitol</i>								
0.00000	0.999257	0.997047	0.994039	0.990356				
0.09889	1.000117	0.997877	0.994840	0.991134	53.36	53.77	54.20	54.61
0.19894	1.000960	0.998688	0.995613	0.991880	53.45	53.87	54.35	54.78
0.29967	1.001786	0.999473	0.996362	0.992607	53.53	53.98	54.47	54.89
0.39481	1.002529	1.000184	0.997038	0.993261	53.64	54.09	54.59	55.01
0.50155	1.003347	1.000961	0.997764	0.993973	53.73	54.19	54.72	55.12
0.59227	1.004018	1.001596	0.998366	0.994550	53.81	54.28	54.81	55.22
0.69637	1.004757	1.002293	0.999045	0.995188	53.91	54.39	54.89	55.33
0.79832	1.005436	1.002952	0.999679	0.995805	54.03	54.49	54.98	55.41
<i>EG + 0.01 mol·kg⁻¹ Sorbitol</i>								
0.00000	0.999887	0.997823	0.994845	0.990914				
0.10112	1.000758	0.998661	0.995656	0.991703	53.42	53.84	54.24	54.65
0.19853	1.001577	0.999445	0.996400	0.992424	53.47	53.91	54.39	54.81

0.29634	1.002374	1.000203	0.997120	0.993124	53.55	54.01	54.51	54.92
0.39843	1.003170	1.000963	0.997841	0.993828	53.66	54.12	54.63	55.03
0.49911	1.003929	1.001682	0.998515	0.994487	53.76	54.23	54.76	55.15
0.59960	1.004676	1.002382	0.999173	0.995115	53.83	54.32	54.86	55.27
0.70270	1.005395	1.003070	0.999836	0.995737	53.94	54.42	54.94	55.38
0.79472	1.006002	1.003645	1.000409	0.996282	54.05	54.53	55.01	55.46
<i>EG + 0.03 mol·kg⁻¹ Sorbitol</i>								
0.00000	1.001172	0.999084	0.996047	0.992106				
0.09897	1.002008	0.999890	0.996825	0.992864	53.53	53.92	54.35	54.74
0.20032	1.002838	1.000690	0.997597	0.993614	53.61	54.01	54.43	54.83
0.29755	1.003605	1.001436	0.998306	0.994300	53.71	54.08	54.54	54.95
0.40096	1.004397	1.002201	0.999032	0.995004	53.80	54.17	54.65	55.06
0.49920	1.005122	1.002891	0.999676	0.995638	53.89	54.28	54.79	55.18
0.60067	1.005859	1.003588	1.000338	0.996269	53.96	54.37	54.88	55.29
0.69838	1.006539	1.004233	1.000950	0.996842	54.04	54.46	54.97	55.41
0.79884	1.007241	1.004866	1.001549	0.997441	54.09	54.56	55.07	55.48
<i>EG + 0.05 mol·kg⁻¹ Sorbitol</i>								
0.00000	1.002435	1.000322	0.997257	0.993322				
0.09873	1.003244	1.001106	0.998011	0.994050	53.72	54.07	54.52	54.97
0.20082	1.004062	1.001892	0.998766	0.994782	53.77	54.15	54.60	55.04

0.29900	1.004830	1.002630	0.999475	0.995463	53.82	54.21	54.66	55.11
0.39980	1.005596	1.003360	1.000176	0.996139	53.88	54.29	54.74	55.19
0.49828	1.006321	1.004060	1.000837	0.996781	53.95	54.35	54.82	55.26
0.60039	1.007057	1.004761	1.001495	0.997427	54.01	54.42	54.91	55.33
0.69943	1.007743	1.005412	1.002101	0.998005	54.08	54.50	55.01	55.44
0.79893	1.008421	1.006037	1.002684	0.998582	54.14	54.59	55.11	55.52
<i>DEG + 0.00 mol·kg⁻¹ Sorbitol</i>								
0.00000	0.999257	0.997047	0.994039	0.990356				
0.09849	1.000689	0.998458	0.995440	0.991758	91.51	91.89	92.23	92.51
0.19736	1.002060	0.999780	0.996778	0.993102	91.72	92.25	92.46	92.71
0.29505	1.003358	1.001026	0.998046	0.994366	91.90	92.50	92.64	92.92
0.41013	1.004837	1.002490	0.999471	0.995788	92.06	92.58	92.85	93.14
0.50063	1.005961	1.003585	1.000531	0.996853	92.17	92.69	93.02	93.31
0.60007	1.007125	1.004735	1.001676	0.997974	92.34	92.83	93.16	93.49
0.69956	1.008278	1.005827	1.002761	0.999056	92.45	92.99	93.32	93.65
0.79993	1.009393	1.006873	1.003829	1.000108	92.57	93.16	93.45	93.80
<i>DEG + 0.01 mol·kg⁻¹ Sorbitol</i>								
0.00000	0.999887	0.997823	0.994845	0.990914				
0.10041	1.001309	0.999210	0.996218	0.992276	91.84	92.35	92.73	93.15
0.19992	1.002670	1.000538	0.997528	0.993586	91.95	92.46	92.86	93.23

0.29515	1.003938	1.001771	0.998738	0.994791	92.03	92.55	92.98	93.35
0.40405	1.005340	1.003137	1.000072	0.996116	92.13	92.65	93.11	93.49
0.49995	1.006534	1.004289	1.001205	0.997240	92.22	92.76	93.22	93.61
0.60913	1.007839	1.005551	1.002445	0.998484	92.34	92.89	93.35	93.72
0.69162	1.008786	1.006456	1.003321	0.999383	92.44	93.01	93.49	93.82
0.79888	1.009988	1.007575	1.004434	1.000525	92.55	93.18	93.64	93.93
<i>DEG + 0.03 mol·kg⁻¹ Sorbitol</i>								
0.00000	1.001172	0.999084	0.996047	0.992106				
0.10000	1.002541	1.000418	0.997357	0.993403	92.21	92.73	93.21	93.66
0.20070	1.003875	1.001719	0.998633	0.994669	92.31	92.82	93.31	93.75
0.29990	1.005146	1.002951	0.999862	0.995884	92.41	92.94	93.36	93.81
0.39776	1.006365	1.004141	1.001040	0.997042	92.49	93.01	93.42	93.89
0.50052	1.007614	1.005356	1.002239	0.998222	92.56	93.08	93.49	93.97
0.60534	1.008851	1.006553	1.003421	0.999401	92.63	93.16	93.57	94.03
0.69708	1.009891	1.007583	1.004438	1.000387	92.71	93.21	93.62	94.11
0.79956	1.011024	1.008693	1.005533	1.001453	92.79	93.28	93.69	94.20
<i>DEG + 0.05 mol·kg⁻¹ Sorbitol</i>								
0.00000	1.002435	1.000322	0.997257	0.993322				
0.10020	1.003759	1.001611	0.998518	0.994571	92.59	93.11	93.64	94.08
0.19977	1.005041	1.002861	0.999738	0.995780	92.64	93.15	93.69	94.13

0.29953	1.006292	1.004082	1.000929	0.996963	92.69	93.19	93.74	94.17
0.39978	1.007510	1.005276	1.002094	0.998122	92.76	93.24	93.79	94.21
0.50150	1.008724	1.006466	1.003241	0.999269	92.80	93.27	93.85	94.25
0.59942	1.009870	1.007579	1.004325	1.000341	92.83	93.31	93.89	94.30
0.69860	1.010999	1.008673	1.005403	1.001411	92.87	93.36	93.92	94.33
0.80042	1.012138	1.009783	1.006485	1.002486	92.90	93.39	93.95	94.36
<i>TEG + 0.00 mol·kg⁻¹ Sorbitol</i>								
0.00000	0.999257	0.997047	0.994039	0.990356				
0.09650	1.001366	0.999126	0.996095	0.992405	128.13	128.69	129.25	129.73
0.20020	1.003551	1.001272	0.998216	0.994520	128.26	128.85	129.42	129.89
0.29205	1.005416	1.003106	1.000013	0.996322	128.38	128.97	129.60	130.03
0.39856	1.007496	1.005140	1.002025	0.998332	128.53	129.15	129.76	130.19
0.49879	1.009367	1.006991	1.003851	1.000147	128.69	129.28	129.89	130.34
0.59989	1.011202	1.008767	1.005625	1.001923	128.84	129.45	130.02	130.46
0.69470	1.012819	1.010377	1.007215	1.003518	128.99	129.59	130.16	130.59
0.79290	1.014471	1.011992	1.008811	1.005119	129.11	129.72	130.29	130.71
<i>TEG + 0.01 mol·kg⁻¹ Sorbitol</i>								
0.00000	0.999887	0.997823	0.994845	0.990914				
0.09989	1.002032	0.999930	0.996931	0.992996	128.44	129.05	129.59	130.06
0.19946	1.004100	1.001952	0.998936	0.995000	128.53	129.18	129.70	130.16

0.30086	1.006132	1.003941	1.000904	0.996967	128.63	129.29	129.82	130.27
0.39136	1.007880	1.005648	1.002605	0.998657	128.74	129.41	129.91	130.39
0.50029	1.009913	1.007647	1.004587	1.000639	128.86	129.51	130.01	130.48
0.59685	1.011659	1.009357	1.006260	1.002321	128.95	129.60	130.14	130.59
0.69910	1.013438	1.011098	1.007983	1.004030	129.06	129.71	130.25	130.72
0.80096	1.015139	1.012777	1.009652	1.005689	129.18	129.81	130.34	130.82

TEG + 0.03 mol·kg⁻¹ Sorbitol

0.00000	1.001172	0.999084	0.996047	0.992106				
0.09945	1.003261	1.001132	0.998074	0.994128	128.78	129.42	129.97	130.45
0.20225	1.005341	1.003177	1.000094	0.996140	128.90	129.51	130.08	130.58
0.30046	1.007259	1.005059	1.001956	0.997991	129.01	129.62	130.18	130.70
0.40037	1.009148	1.006898	1.003790	0.999810	129.10	129.75	130.27	130.81
0.50006	1.010952	1.008668	1.005544	1.001569	129.23	129.87	130.39	130.90
0.60023	1.012708	1.010393	1.007253	1.003267	129.34	129.97	130.49	131.01
0.69798	1.014346	1.012024	1.008842	1.004857	129.47	130.06	130.62	131.13
0.79686	1.015964	1.013605	1.010405	1.006421	129.57	130.17	130.73	131.23

TEG + 0.05 mol·kg⁻¹ Sorbitol

0.00000	1.002435	1.000322	0.997257	0.993322				
0.09971	1.004487	1.002339	0.999249	0.995296	129.07	129.65	130.24	130.86
0.20032	1.006484	1.004300	1.001191	0.997217	129.18	129.77	130.33	130.97

0.29848	1.008368	1.006139	1.003019	0.999020	129.27	129.90	130.43	131.09
0.40106	1.010260	1.007997	1.004862	1.000847	129.39	130.01	130.53	131.18
0.49992	1.012023	1.009731	1.006571	1.002528	129.49	130.1	130.64	131.31
0.59987	1.013740	1.011425	1.008225	1.004179	129.60	130.19	130.77	131.41
0.69799	1.015376	1.013018	1.009792	1.005749	129.69	130.30	130.89	131.50
0.79874	1.016973	1.014605	1.011336	1.007308	129.82	130.40	131.02	131.59

^a m_A is the molality of glycols in aqueous sorbitol solutions; Standard uncertainties u are $u(m) = 2 \times 10^{-5}$ mol.kg⁻¹, $u(T) = 0.001$ K, $u(\rho) = 0.05$ kg.m⁻³ and $u(p) = 0.01$ MPa.

Table 4.20Limiting apparent molar volumes, V_{ϕ}° , and experimental slopes, S_V^* of glycols in aqueous solutions of sorbitol at different temperatures.

${}^a m_B$ (mol·kg ⁻¹)	$V_{\phi}^{\circ} \times 10^6$ (m ³ ·mol ⁻¹)					$S_V^* \times 10^6$ (m ³ ·kg·mol ⁻²)				
	$T = 288.15$ K	$T = 298.15$ K	$T = 308.15$ K	$T = 318.15$ K	$T = 288.15$ K	$T = 298.15$ K	$T = 308.15$ K	$T = 318.15$ K	$T = 308.15$ K	$T = 318.15$ K
EG										
0.00	53.26(±0.008)	53.67(±0.005)	54.13(±0.023)	54.54(±0.020)	0.95(±0.017)	1.03(±0.009)	1.11(±0.046)	1.13(±0.040)	1.11(±0.046)	1.13(±0.040)
0.01	53.30(±0.015)	53.72(±0.009)	54.17(±0.025)	54.57(±0.015)	0.92(±0.030)	1.00(±0.017)	1.11(±0.049)	1.16(±0.030)	1.11(±0.049)	1.16(±0.030)
0.03	53.46(±0.013)	53.82(±0.008)	54.23(±0.012)	54.62(±0.011)	0.82(±0.026)	0.92(±0.016)	1.06(±0.024)	1.10(±0.022)	1.06(±0.024)	1.10(±0.022)
0.05	53.65(±0.007)	54.00(±0.007)	54.42(±0.013)	54.88(±0.010)	0.61(±0.013)	0.72(±0.014)	0.83(±0.026)	0.78(±0.021)	0.83(±0.026)	0.78(±0.021)
DEG										
0.00	91.42(±0.029)	91.88(±0.069)	92.11(±0.028)	92.36(±0.021)	1.48(±0.057)	1.62(±0.137)	1.73(±0.056)	1.85(±0.042)	1.73(±0.056)	1.85(±0.042)
0.01	91.73(±0.010)	92.21(±0.023)	92.60(±0.013)	93.02(±0.010)	1.01(±0.019)	1.15(±0.045)	1.28(±0.025)	1.15(±0.020)	1.28(±0.025)	1.15(±0.020)
0.03	92.15(±0.011)	92.68(±0.017)	93.16(±0.008)	93.59(±0.007)	0.81(±0.022)	0.78(±0.034)	0.67(±0.016)	0.75(±0.014)	0.67(±0.016)	0.75(±0.014)
0.05	92.56(±0.012)	93.07(±0.004)	93.60(±0.010)	94.05(±0.005)	0.45(±0.023)	0.40(±0.008)	0.46(±0.020)	0.40(±0.011)	0.46(±0.020)	0.40(±0.011)
TEG										
0.00	127.97(±0.011)	128.55(±0.008)	129.14(±0.020)	129.61(±0.013)	1.44(±0.021)	1.49(±0.015)	1.48(±0.039)	1.41(±0.026)	1.48(±0.039)	1.41(±0.026)
0.01	128.32(±0.007)	128.96(±0.012)	129.49(±0.008)	129.95(±0.008)	1.06(±0.013)	1.07(±0.024)	1.08(±0.016)	1.09(±0.016)	1.08(±0.016)	1.09(±0.016)
0.03	128.66(±0.008)	129.30(±0.010)	129.85(±0.010)	130.35(±0.009)	1.14(±0.016)	1.10(±0.020)	1.08(±0.019)	1.10(±0.017)	1.08(±0.019)	1.10(±0.017)
0.05	128.96(±0.006)	129.56(±0.012)	130.10(±0.015)	130.76(±0.010)	1.06(±0.013)	1.06(±0.024)	1.12(±0.030)	1.06(±0.021)	1.12(±0.030)	1.06(±0.021)

^a m_B is the molality of aqueous solutions of sorbitol.

Table 4.21

Partial molar volume of transfer, ΔV_{ϕ}^o of glycols in aqueous solutions of sorbitol at different temperatures.

${}^a m_B$ (mol·kg ⁻¹)	$\Delta V_{\phi}^o \times 10^6$ (m ³ ·mol ⁻¹)			
	$T = 288.15$ K	$T = 298.15$ K	$T = 308.15$ K	$T = 318.15$ K
EG				
0.01	0.04	0.05	0.04	0.02
0.03	0.20	0.15	0.11	0.08
0.05	0.39	0.33	0.29	0.34
DEG				
0.01	0.31	0.33	0.48	0.66
0.03	0.73	0.80	1.05	1.23
0.05	1.14	1.19	1.49	1.69
TEG				
0.01	0.35	0.42	0.35	0.33
0.03	0.69	0.76	0.71	0.74
0.05	0.99	1.02	0.96	1.15

${}^a m_B$ is the molality of aqueous solutions of sorbitol.

Table 4.22

Values of empirical parameters of equation 4.4 for glycols in aqueous glycerol solutions.

${}^a m_B$ (mol·kg ⁻¹)	$A \times 10^6$ (m ³ ·mol ⁻¹)	$B \times 10^6$ (m ³ ·mol ⁻¹ ·K ⁻¹)	$C \times 10^6$ (m ³ ·mol ⁻¹ ·K ⁻²)	R^2	ARD
EG					
0.00	53.68	0.043	0.000002	0.9999	0.00017
0.01	53.73	0.043	-0.0001	0.9999	0.00014
0.03	53.83	0.038	0.0001	0.9999	0.00015
0.05	54.00	0.039	0.0003	0.9999	0.00007
DEG					
0.00	91.84	0.036	-0.0005	0.9999	0.00026
0.01	92.19	0.044	-0.0001	0.9999	0.00014
0.03	92.68	0.050	-0.0002	0.9999	0.000001
0.05	93.09	0.052	-0.0002	0.9999	0.00012
TEG					
0.00	128.57	0.058	-0.0002	0.9999	0.00011
0.01	128.96	0.058	-0.0005	0.9999	0.00005
0.03	129.30	0.060	-0.0003	0.9999	0.00003
0.05	129.54	0.058	0.0001	0.9999	0.00015

^a m_B is the molality of aqueous solutions of sorbitol.

Table 4.23

Limiting apparent molar expansibilities, E_{ϕ}^0 for glycols in aqueous glycerol solutions at different temperatures.

${}^a m_B$ (mol·kg ⁻¹)	$E_{\phi}^0 \times 10^6$ (m ³ ·mol ⁻¹ ·K ⁻¹)				$(\partial E_{\phi}^0 / \partial T)_p$ (m ³ ·mol ⁻¹ ·K ⁻²)
	$T = 288.15$ K	$T = 298.15$ K	$T = 308.15$ K	$T = 318.15$ K	
EG					
0.00	0.0430	0.0430	0.0431	0.0431	0.000005
0.01	0.0445	0.0432	0.0418	0.0404	-0.0001
0.03	0.0376	0.0383	0.0391	0.0399	0.0002
0.05	0.0331	0.0385	0.0440	0.0494	0.0005
DEG					
0.00	0.0464	0.0357	0.0250	0.0144	-0.0011
0.01	0.0464	0.0437	0.0411	0.0384	-0.0003
0.03	0.0529	0.0504	0.0480	0.0455	-0.0005
0.05	0.0552	0.0518	0.0483	0.0448	-0.0003
TEG					
0.00	0.0625	0.0576	0.0526	0.0477	-0.0005
0.01	0.0675	0.0585	0.0494	0.0403	-0.0009
0.03	0.0631	0.0597	0.0562	0.0528	-0.0007
0.05	0.0551	0.0580	0.0609	0.0638	0.0003

^a m_B is the molality of aqueous solutions of sorbitol.

Table 4.24

Values of speed of sound, c , and apparent molar isentropic compression, $K_{\phi,s}$ of glycols in aqueous solutions of sorbitol at different temperatures and experimental pressure, $p = 0.1$ MPa.

$^a m_A$ (mol·kg ⁻¹)	c (m·s ⁻¹)				$K_{\phi,s} \times 10^6$ (m ³ ·mol ⁻¹ ·GPa ⁻¹)			
	$T = 288.15$ K	$T = 298.15$ K	$T = 308.15$ K	$T = 318.15$ K	$T = 288.15$ K	$T = 298.15$ K	$T = 308.15$ K	$T = 318.15$ K
<i>EG + 0.00 mol·kg⁻¹ Sorbitol</i>								
0.00000	1466.59	1495.85	1519.14	1536.02				
0.09889	1469.57	1498.92	1521.84	1539.17	-46.06	-44.28	-42.93	-41.98
0.19894	1472.72	1501.72	1524.03	1542.24	-46.34	-44.54	-43.18	-42.23
0.29967	1475.45	1504.29	1526.18	1544.95	-46.46	-44.65	-43.29	-42.34
0.39481	1478.57	1506.64	1528.28	1547.87	-46.53	-44.72	-43.35	-42.40
0.50155	1481.17	1509.09	1530.34	1550.65	-46.59	-44.78	-43.41	-42.46
0.59227	1484.02	1511.61	1534.12	1553.56	-46.64	-44.82	-43.45	-42.49
0.69637	1486.59	1514.81	1537.56	1556.55	-46.68	-44.86	-43.49	-42.53
0.79832	1489.45	1517.93	1540.35	1559.58	-46.72	-44.90	-43.52	-42.57
<i>EG + 0.01 mol·kg⁻¹ Sorbitol</i>								
0.00000	1467.84	1497.55	1520.61	1537.24				
0.10112	1470.98	1500.61	1523.56	1540.37	-46.00	-44.19	-42.85	-41.93
0.19853	1473.92	1503.51	1526.27	1543.25	-46.26	-44.44	-43.10	-42.17
0.29634	1476.85	1506.35	1529.12	1546.09	-46.37	-44.55	-43.20	-42.27
0.39843	1480.02	1509.22	1532.18	1548.91	-46.45	-44.62	-43.27	-42.34

0.49911	1482.52	1511.85	1534.69	1551.57	-46.51	-44.68	-43.32	-42.39
0.59960	1485.58	1514.98	1538.05	1554.86	-46.56	-44.72	-43.37	-42.43
0.70270	1488.75	1518.29	1541.61	1558.21	-46.61	-44.76	-43.40	-42.46
0.79472	1491.03	1520.69	1544.15	1560.62	-46.64	-44.80	-43.44	-42.49

EG + 0.03 mol·kg⁻¹ Sorbitol

0.00000	1469.89	1499.13	1522.05	1538.75				
0.09897	1472.91	1502.18	1524.89	1541.78	-45.86	-44.08	-42.76	-41.84
0.20032	1476.06	1505.54	1527.85	1544.69	-46.13	-44.35	-43.02	-42.09
0.29755	1478.85	1508.12	1530.54	1547.34	-46.24	-44.45	-43.12	-42.19
0.40096	1482.03	1511.35	1533.96	1550.48	-46.32	-44.53	-43.19	-42.25
0.49920	1484.79	1514.17	1536.73	1553.32	-46.38	-44.58	-43.24	-42.30
0.60067	1487.58	1516.87	1539.62	1556.18	-46.43	-44.62	-43.28	-42.34
0.69838	1490.08	1519.92	1542.56	1558.98	-46.47	-44.66	-43.32	-42.38
0.79884	1492.8	1522.81	1545.67	1562.06	-46.51	-44.70	-43.35	-42.41

EG + 0.05 mol·kg⁻¹ Sorbitol

0.00000	1472.54	1501.21	1523.28	1540.42				
0.09873	1475.48	1504.26	1526.17	1543.36	-45.69	-43.96	-42.69	-41.74
0.20082	1478.69	1507.53	1529.32	1546.37	-45.97	-44.22	-42.95	-41.99
0.29900	1481.68	1510.29	1532.23	1549.26	-46.08	-44.33	-43.05	-42.09
0.39980	1484.59	1513.06	1535.14	1552.08	-46.15	-44.40	-43.12	-42.16
0.49828	1487.39	1515.74	1537.95	1554.93	-46.21	-44.45	-43.17	-42.21
0.60039	1490.13	1518.61	1540.85	1557.89	-46.26	-44.50	-43.21	-42.25

0.69943	1492.84	1521.55	1543.85	1560.66	-46.30	-44.54	-43.25	-42.28
0.79893	1495.35	1524.33	1546.86	1563.68	-46.34	-44.57	-43.28	-42.31
<i>DEG + 0.00 mol·kg⁻¹ Sorbitol</i>								
0.00000	1466.59	1495.85	1519.14	1536.02				
0.09849	1472.11	1501.24	1523.52	1541.59	-46.09	-44.30	-42.95	-42.01
0.19736	1478.01	1506.01	1527.52	1547.17	-46.39	-44.59	-43.23	-42.29
0.29505	1483.78	1510.78	1531.47	1552.68	-46.53	-44.72	-43.36	-42.41
0.41013	1489.36	1516.15	1536.11	1558.07	-46.64	-44.83	-43.46	-42.52
0.50063	1494.73	1520.34	1541.59	1563.21	-46.72	-44.90	-43.53	-42.58
0.60007	1500.28	1527.06	1549.18	1568.76	-46.79	-44.97	-43.60	-42.64
0.69956	1505.69	1534.55	1556.59	1573.92	-46.85	-45.02	-43.65	-42.70
0.79993	1510.78	1540.32	1562.29	1579.48	-46.91	-45.08	-43.71	-42.75
<i>DEG + 0.01 mol·kg⁻¹ Sorbitol</i>								
0.00000	1467.84	1497.55	1520.61	1537.24				
0.10041	1473.34	1502.97	1526.18	1542.89	-46.02	-44.21	-42.88	-41.95
0.19992	1479.22	1508.73	1531.46	1548.34	-46.32	-44.49	-43.15	-42.22
0.29515	1484.81	1513.85	1536.28	1553.65	-46.45	-44.62	-43.27	-42.34
0.40405	1490.84	1519.72	1541.92	1559.52	-46.56	-44.72	-43.37	-42.44
0.49995	1496.15	1524.82	1547.29	1564.61	-46.63	-44.79	-43.44	-42.51
0.60913	1502.08	1530.95	1553.17	1570.52	-46.71	-44.87	-43.51	-42.57
0.69162	1506.43	1535.53	1557.54	1574.92	-46.76	-44.92	-43.56	-42.62

0.79888	1512.08	1541.58	1563.68	1580.81	-46.83	-44.97	-43.61	-42.68
<i>DEG + 0.03 mol·kg⁻¹ Sorbitol</i>								
0.00000	1469.89	1499.13	1522.05	1538.75				
0.10000	1475.27	1504.86	1527.55	1544.53	-45.89	-44.11	-42.79	-41.86
0.20070	1480.96	1510.78	1532.72	1549.97	-46.18	-44.40	-43.07	-42.13
0.29990	1486.75	1516.24	1538.05	1555.38	-46.32	-44.52	-43.19	-42.26
0.39776	1492.33	1521.52	1543.05	1560.81	-46.41	-44.61	-43.28	-42.34
0.50052	1497.98	1526.69	1548.55	1566.22	-46.49	-44.69	-43.35	-42.41
0.60534	1503.55	1532.53	1554.35	1571.94	-46.57	-44.76	-43.42	-42.48
0.69708	1508.59	1537.56	1559.12	1577.02	-46.63	-44.81	-43.47	-42.53
0.79956	1514.24	1543.46	1565.07	1582.35	-46.69	-44.87	-43.53	-42.58
<i>DEG + 0.05 mol·kg⁻¹ Sorbitol</i>								
0.00000	1472.54	1501.21	1523.28	1540.42				
0.10020	1477.82	1506.89	1528.94	1546.18	-45.72	-43.99	-42.72	-41.77
0.19977	1483.33	1512.64	1534.11	1551.62	-46.01	-44.27	-42.99	-42.04
0.29953	1488.96	1518.27	1539.52	1557.04	-46.15	-44.40	-43.11	-42.16
0.39978	1494.75	1523.62	1544.63	1562.58	-46.24	-44.49	-43.20	-42.24
0.50150	1500.33	1528.92	1550.02	1567.94	-46.32	-44.56	-43.27	-42.31
0.59942	1505.64	1534.48	1555.52	1573.24	-46.39	-44.62	-43.33	-42.37
0.69860	1511.04	1539.87	1560.65	1578.56	-46.45	-44.68	-43.39	-42.43
0.80042	1516.68	1545.83	1566.42	1583.98	-46.51	-44.74	-43.44	-42.48

TEG + 0.00 mol·kg⁻¹ Sorbitol

0.00000	1466.59	1495.85	1519.14	1536.02					
0.09650	1474.72	1503.48	1525.09	1543.95	-46.12	-44.33	-42.97	-42.03	
0.20020	1483.26	1511.04	1531.28	1552.21	-46.47	-44.66	-43.30	-42.35	
0.29205	1491.74	1517.62	1536.87	1560.57	-46.63	-44.82	-43.45	-42.50	
0.39856	1499.22	1525.38	1543.31	1567.78	-46.77	-44.95	-43.57	-42.62	
0.49879	1508.48	1532.21	1550.94	1576.89	-46.88	-45.05	-43.68	-42.72	
0.59989	1516.07	1542.37	1563.23	1584.48	-46.98	-45.15	-43.77	-42.81	
0.69470	1523.59	1551.24	1572.72	1592.31	-47.06	-45.23	-43.85	-42.89	
0.79290	1531.19	1560.56	1582.65	1600.48	-47.15	-45.31	-43.93	-42.97	

TEG + 0.01 mol·kg⁻¹ Sorbitol

0.00000	1467.84	1497.55	1520.61	1537.24					
0.09989	1476.72	1505.85	1528.45	1545.45	-46.06	-44.24	-42.91	-41.98	
0.19946	1485.02	1514.25	1535.98	1553.54	-46.38	-44.56	-43.21	-42.28	
0.30086	1493.31	1522.16	1543.94	1561.78	-46.56	-44.72	-43.37	-42.44	
0.39136	1500.78	1529.37	1551.14	1569.02	-46.67	-44.83	-43.48	-42.54	
0.50029	1509.82	1537.95	1559.92	1577.78	-46.79	-44.95	-43.59	-42.65	
0.59685	1517.59	1545.53	1567.85	1585.65	-46.89	-45.04	-43.68	-42.74	
0.69910	1525.52	1553.81	1576.53	1593.99	-46.98	-45.13	-43.76	-42.82	
0.80096	1533.56	1562.87	1584.83	1602.56	-47.07	-45.21	-43.84	-42.90	

TEG + 0.03 mol·kg⁻¹ Sorbitol

0.00000	1469.89	1499.13	1522.05	1538.75					
0.09945	1478.42	1507.29	1529.78	1546.92	-45.92	-44.15	-42.82	-41.90	
0.20225	1486.99	1515.98	1537.56	1555.32	-46.26	-44.46	-43.13	-42.20	
0.30046	1495.23	1523.75	1545.37	1563.23	-46.42	-44.62	-43.28	-42.35	
0.40037	1503.52	1531.62	1553.46	1571.17	-46.54	-44.74	-43.40	-42.46	
0.50006	1511.71	1539.56	1561.38	1579.24	-46.65	-44.84	-43.50	-42.56	
0.60023	1519.77	1547.42	1569.69	1587.16	-46.75	-44.93	-43.58	-42.64	
0.69798	1527.28	1555.35	1577.93	1595.18	-46.83	-45.01	-43.66	-42.72	
0.79686	1534.85	1564.18	1585.86	1603.29	-46.92	-45.09	-43.74	-42.80	
<i>TEG + 0.05 mol·kg⁻¹ Sorbitol</i>									
0.00000	1472.54	1501.21	1523.28	1540.42					
0.09971	1480.95	1509.34	1531.24	1548.54	-45.76	-44.02	-42.75	-41.80	
0.20032	1489.59	1517.93	1538.88	1556.78	-46.08	-44.33	-43.06	-42.10	
0.29848	1497.84	1525.61	1546.63	1564.61	-46.24	-44.49	-43.21	-42.25	
0.40106	1506.23	1533.72	1554.73	1572.99	-46.37	-44.61	-43.32	-42.36	
0.49992	1514.49	1541.57	1562.64	1580.82	-46.47	-44.71	-43.42	-42.45	
0.59987	1522.36	1549.37	1570.88	1588.93	-46.57	-44.80	-43.50	-42.54	
0.69799	1529.89	1557.35	1579.14	1596.74	-46.65	-44.88	-43.58	-42.61	
0.79874	1537.51	1566.35	1587.25	1604.94	-46.74	-44.96	-43.66	-42.69	

^a m_A is the molality of glycols in aqueous sorbitol solutions; Standard uncertainties u are $u(m) = 2 \times 10^{-5} \text{ mol} \cdot \text{kg}^{-1}$, $u(T) = 0.001 \text{ K}$, $u(c) = 0.05 \text{ m} \cdot \text{s}^{-1}$ and $u(p) = 0.01 \text{ MPa}$.

Table 4.25

Limiting apparent molar isentropic compression, $K_{\phi,s}^0$, and experimental slope, S_K^* for glycols in aqueous solutions of sorbitol at different temperatures.

${}^a m_B$ (mol·kg ⁻¹)	$K_{\phi,s}^0 \times 10^6$ (m ³ ·mol ⁻¹ ·GPa ⁻¹)				$S_K^* \times 10^6$ (kg·m ³ ·mol ⁻² ·GPa ⁻¹)			
	$T = 288.15$ K	$T = 298.15$ K	$T = 308.15$ K	$T = 318.15$ K	$T = 288.15$ K	$T = 298.15$ K	$T = 308.15$ K	$T = 318.15$ K
EG								
0.00	-46.13(±0.066)	-44.34(±0.063)	-42.99(±0.062)	-42.05(±0.061)	-0.83(±0.131)	-0.78(±0.126)	-0.75(±0.123)	-0.73(±0.121)
0.01	-46.06(±0.063)	-44.25(±0.061)	-42.91(±0.059)	-41.99(±0.059)	-0.82(±0.126)	-0.77(±0.121)	-0.73(±0.118)	-0.71(±0.116)
0.03	-45.93(±0.065)	-44.15(±0.063)	-42.83(±0.061)	-41.90(±0.061)	-0.81(±0.128)	-0.77(±0.125)	-0.73(±0.122)	-0.71(±0.120)
0.05	-45.76(±0.065)	-44.03(±0.062)	-42.76(±0.061)	-41.81(±0.060)	-0.81(±0.128)	-0.76(±0.124)	-0.73(±0.122)	-0.71(±0.119)
DEG								
0.00	-46.14(±0.069)	-44.35(±0.066)	-43.00(±0.065)	-42.06(±0.064)	-1.06(±0.136)	-1.00(±0.131)	-0.98(±0.129)	-0.96(±0.127)
0.01	-46.07(±0.066)	-44.26(±0.064)	-42.92(±0.063)	-42.00(±0.061)	-1.04(±0.132)	-0.99(±0.127)	-0.95(±0.124)	-0.94(±0.122)
0.03	-45.94(±0.065)	-44.16(±0.062)	-42.84(±0.061)	-41.91(±0.060)	-1.03(±0.129)	-0.98(±0.124)	-0.94(±0.121)	-0.92(±0.119)
0.05	-45.77(±0.063)	-44.04(±0.061)	-42.77(±0.060)	-41.82(±0.059)	-1.01(±0.126)	-0.96(±0.122)	-0.93(±0.119)	-0.91(±0.117)
TEG								
0.00	-46.15(±0.073)	-44.36(±0.070)	-43.00(±0.068)	-42.06(±0.067)	-1.36(±0.145)	-1.29(±0.140)	-1.25(±0.136)	-1.23(±0.134)
0.01	-46.08(±0.068)	-44.26(±0.065)	-42.93(±0.064)	-42.00(±0.063)	-1.34(±0.134)	-1.27(±0.129)	-1.23(±0.126)	-1.21(±0.125)
0.03	-45.95(±0.069)	-44.17(±0.066)	-42.85(±0.065)	-41.92(±0.064)	-1.30(±0.136)	-1.24(±0.131)	-1.20(±0.128)	-1.18(±0.126)
0.05	-45.78(±0.067)	-44.05(±0.065)	-42.78(±0.064)	-41.83(±0.062)	-1.28(±0.133)	-1.22(±0.128)	-1.18(±0.126)	-1.16(±0.123)

^a m_B is the molality of aqueous solutions of sorbitol.

Table 4.26

Partial molar isentropic compression of transfer, $\Delta K_{\phi,s}^o$ of glycols in aqueous solutions of sorbitol at different temperatures.

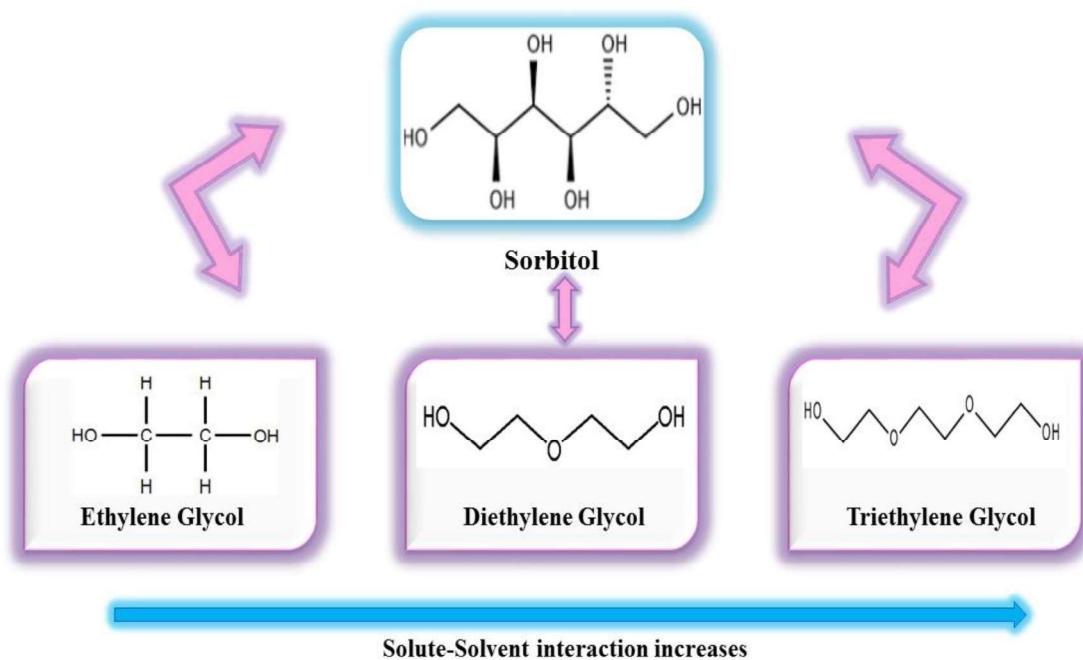
${}^a m_B$ (mol·kg ⁻¹)	$\Delta K_{\phi,s}^o \times 10^6$ (m ³ ·mol ⁻¹ ·GPa ⁻¹)			
	$T = 288.15$ K	$T = 298.15$ K	$T = 308.15$ K	$T = 318.15$ K
EG				
0.01	0.07	0.10	0.08	0.06
0.03	0.21	0.19	0.16	0.15
0.05	0.37	0.32	0.23	0.24
DEG				
0.01	0.07	0.10	0.08	0.06
0.03	0.20	0.19	0.16	0.15
0.05	0.37	0.32	0.23	0.24
TEG				
0.01	0.07	0.09	0.07	0.06
0.03	0.20	0.18	0.15	0.14
0.05	0.36	0.31	0.22	0.23

${}^a m_B$ is the molality of aqueous solutions of sorbitol.

Table 4.27

Pair and triplet interaction coefficients of glycols in aqueous solutions of sorbitol at different temperatures.

T/K	$V_{AB} \times 10^6$ (m ³ ·mol ⁻² ·kg)	$V_{ABB} \times 10^6$ (m ³ ·mol ⁻³ ·kg ²)	$K_{AB} \times 10^6$ (m ³ ·mol ⁻² ·kg·GPa ⁻¹)	$K_{ABB} \times 10^6$ (m ³ ·mol ⁻³ ·kg ² ·GPa ⁻¹)
EG				
288.15	2.17	23.04	3.22	6.41
298.15	1.65	21.22	3.92	-10.71
308.15	0.59	30.60	3.62	-17.57
318.15	-0.86	56.11	2.79	-5.45
DEG				
288.15	14.43	-42.00	3.20	6.72
298.15	16.19	-57.88	3.90	-10.39
308.15	22.96	-108.92	3.63	-17.56
318.15	29.70	-173.95	2.87	-6.26
TEG				
288.15	15.75	-79.77	2.99	8.30
298.15	18.68	-115.42	3.71	-9.03
308.15	16.64	-94.51	3.39	-15.80
318.15	15.09	-48.90	2.59	-3.96



Scheme 2: EG / DEG/ TEG and Sorbitol interactions.

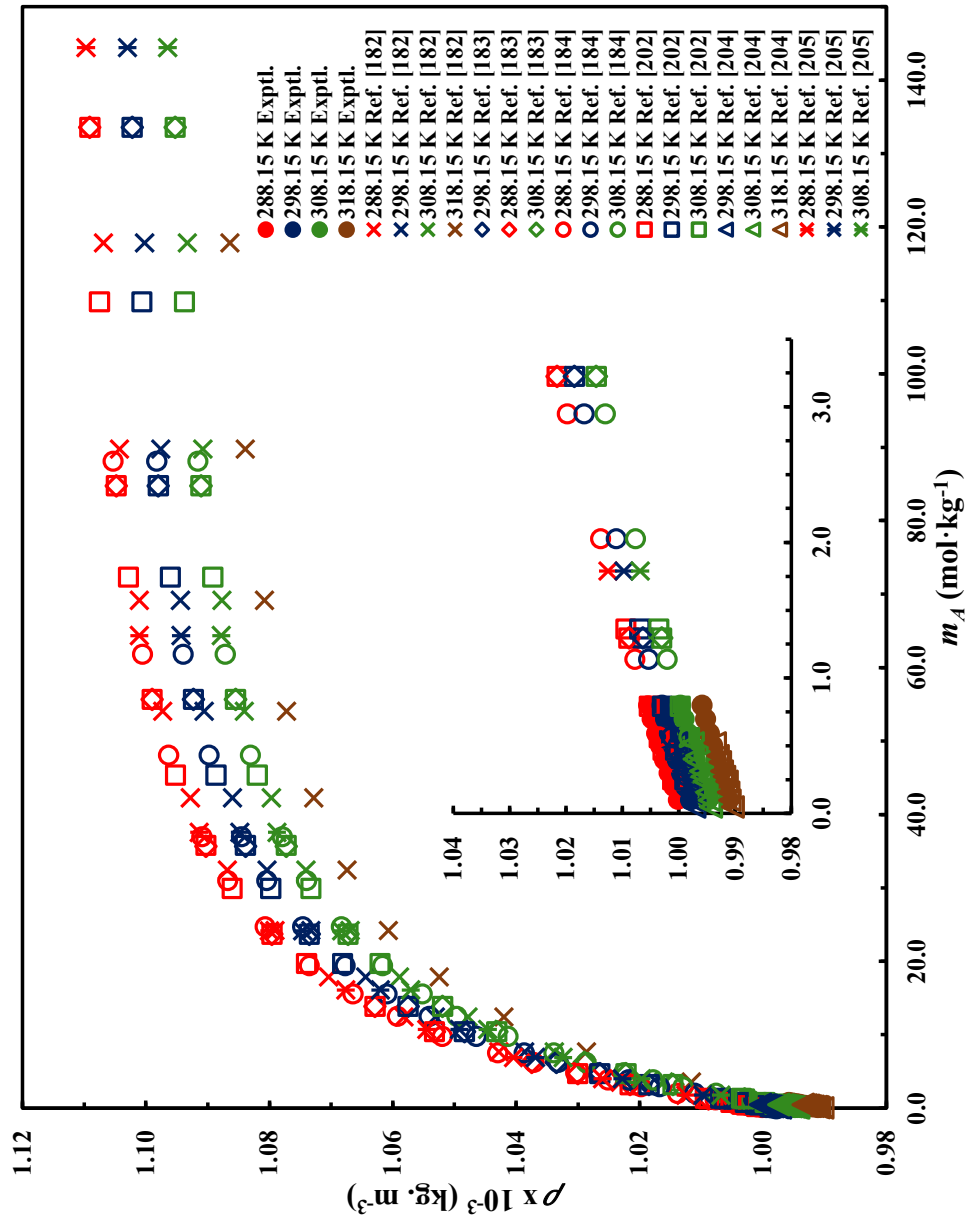


Figure 4.20: Plots of experimental and literature values [182-188, 202, 204-206] of densities for (ethylene glycol + water) mixtures water at different temperatures.

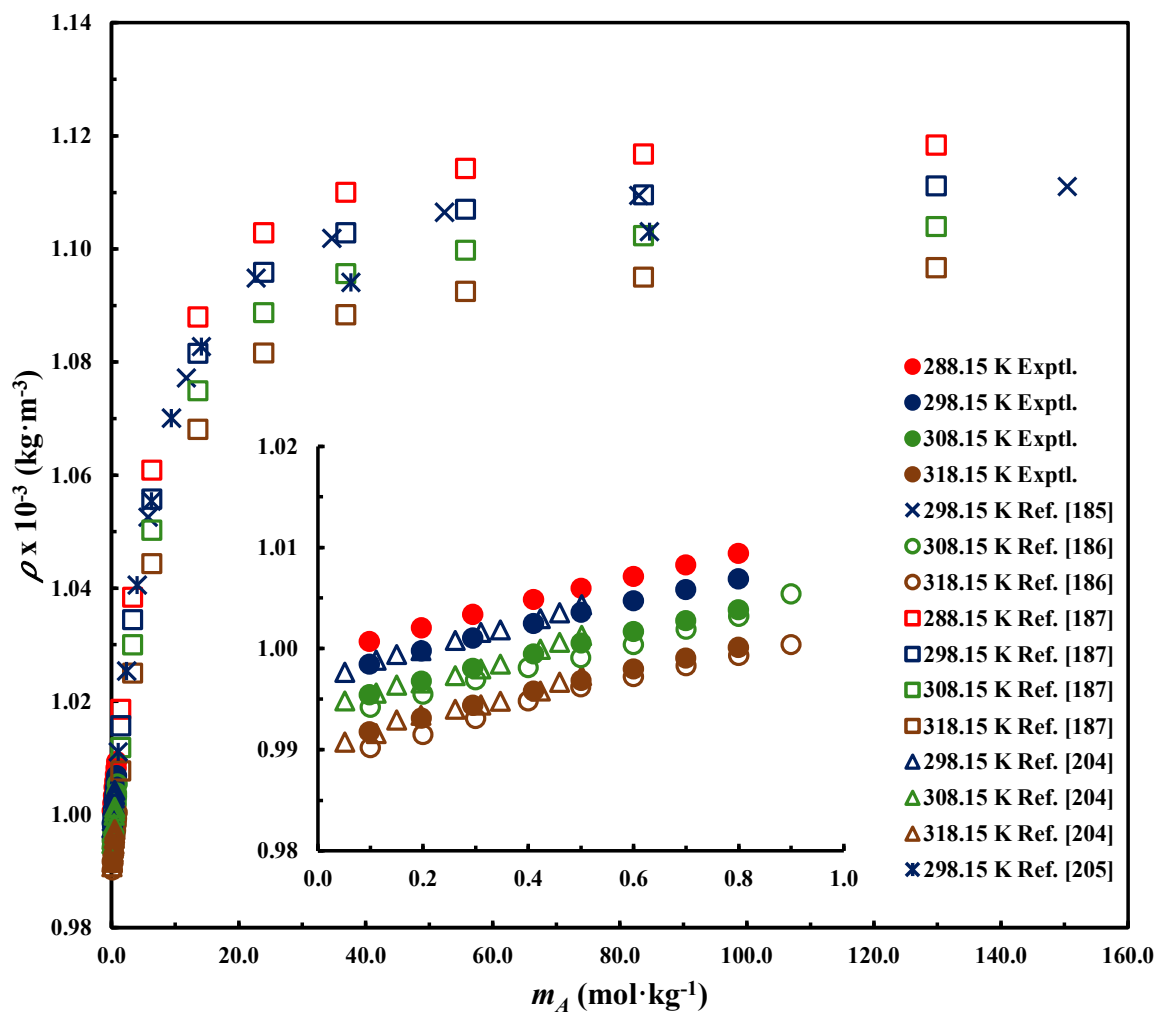


Figure 4.21: Plots of experimental and literature values [185-187, 204, 205] of densities for (diethylene glycol+ water) mixtures at different temperatures.

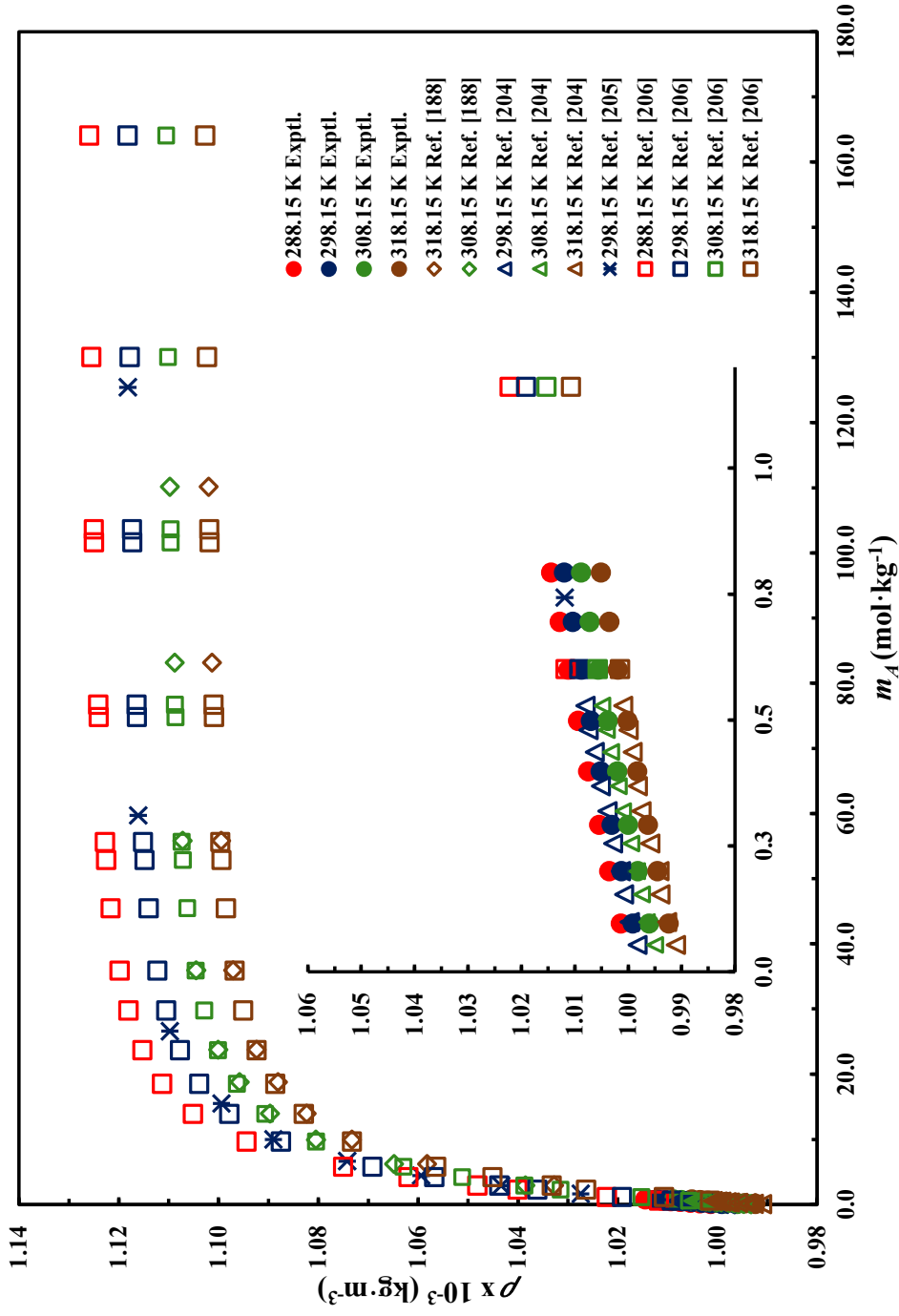


Figure 4.22: Plots of experimental and literature values [188, 204-206] of densities for (triethylene glycol+ water) mixtures at different temperatures.

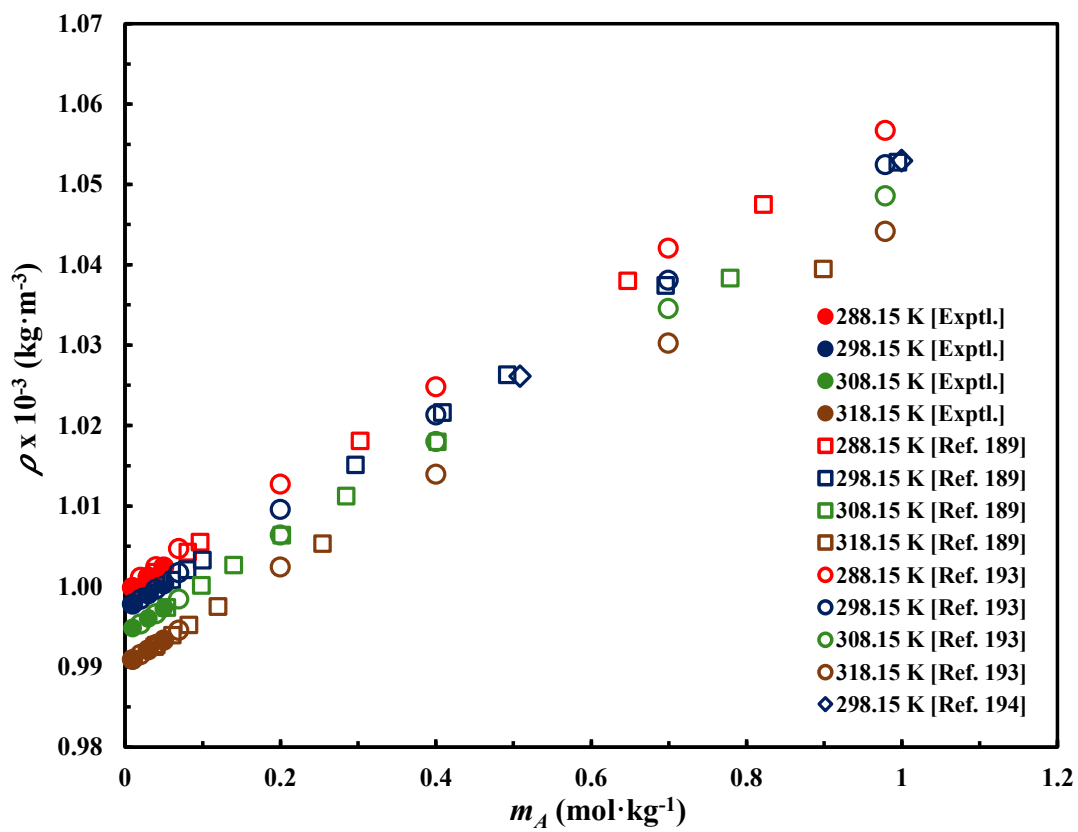


Figure 4.23: Plots of experimental and literature values [189, 193, 194] of densities for (sorbitol+ water) mixtures at different temperatures.

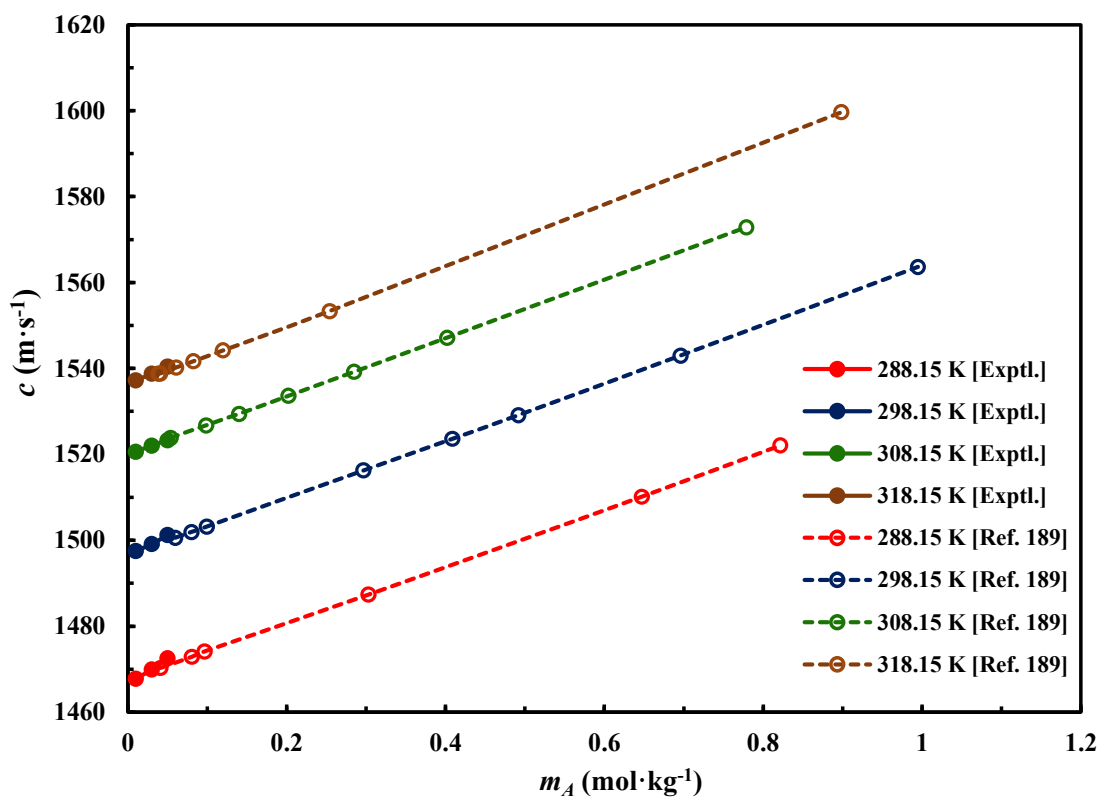


Figure 4.24: Plots of experimental and literature values [189] of ultrasonic velocities for (sorbitol+ water) mixtures at different temperatures.

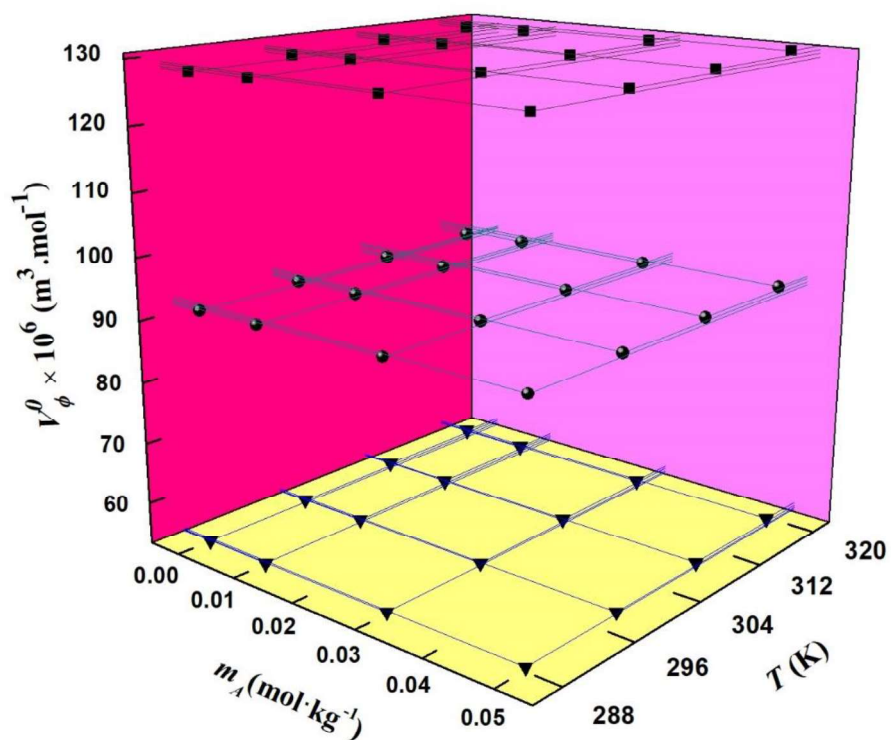


Figure 4.25: Plots of partial molar volume V_ϕ^o for ethylene glycol (▲), diethylene glycol (●) and triethylene glycol (■) in different concentrations of aqueous sorbitol solutions at different temperatures.

Section IV

In continuation to our earlier sections with sugar alcohols, in the present section we have studied two PEGs, polyethylene glycol-400 and polyethylene glycol-4000 in aqueous solutions of sorbitol at different concentrations and temperatures.

Density

The densities, ρ for PEG-400 and PEG-4000 in (0.00, 0.01, 0.03, 0.05) mol·kg⁻¹ aqueous sorbitol solutions are attained at different temperatures ($T = 288.15$ - 318.15) K and are indexed in Table 4.28. It has been professed from the data that the density values are rising with respect to concentration of PEGs as well as sorbitol. But at a specific sorbitol's concentration, the values of density are falling relating to temperature. The experimental density values for aqueous PEGs mixtures at different temperatures have been compared with literature values [95, 118, 123, 200, 201] and the comparison is shown by graphs in Figures 4.26 and 4.27. From 4.26 and 4.27, it is clear that the experimental values are in coherence with literature values.

Apparent molar volume

The obtained density values are utilized to compute the apparent molar volumes V_ϕ , using equation 4.1. The computed apparent molar volumes are attributed in Table 4.28 and all the values are found to be positive. With rising concentration of sorbitol, the V_ϕ values tend to increase. Also, at a specific sorbitol's concentration, the upsurge in V_ϕ values are noticed with respect to upsurge in molality of PEGs and temperature which infers pronounced solute-solvent interactions. Similarly, the surge in values of V_ϕ is seen in reference to molecular mass of PEGs that is along with escalating molecular mass of PEGs, apparent molar volumes escalate as well as for entire temperature range and at entire sorbitol's concentrations ensuing extremum solute-solvent interaction in PEG-4000. This enhancement in V_ϕ values can be accredited to various forces such as dipole-induced dipole, dipole-dipole interactions and various factors namely hydrophobic hydration in water-rich region, hydrophilic effect [146].

Partial molar volume

By the means of least squares fitting of apparent molar volume, partial molar volume V_{ϕ}^0 is calculated from equation 4.2. In Table 4.29 the values of V_{ϕ}^0 and S_V^* along with standard deviations are provided. The standard deviations are evaluated from V_{ϕ} values by least squares fitting of it to equation 4.2. The entire values of V_{ϕ}^0 are positive and rise with escalation in concentration of sorbitol and temperature in both PEGs as epitomized in Figure 4.28. Further at individual temperature, the values of V_{ϕ}^0 upsurge with respect to molecular mass of PEGs resulting in highest values for PEG-4000 which further intimates intensified solute-solvent interactions for PEG-4000 as compared to PEG-400. This surge in V_{ϕ}^0 values can be accredited to strong hydrogen bond interactions among the oxygen atoms of PEGs and hydrogen atoms of water. The packaging effects (upon mixing, the comparatively trivial water molecules fit into the free volume available for PEGs) also contributes to rising V_{ϕ}^0 values [200]. From the definition, the partial molar volumes are sovereign of solute-solute interaction, therefore delivers knowledge regarding solute-solvent interactions [202]. The variation in V_{ϕ}^0 values of PEG-400 and PEG-4000 is very high which acclaims that interaction among unlike molecules is dreadfully susceptible by the size of hydrocarbon chain [91]. Furthermore, from Table 4.29, the magnitude of S_V^* for whole concentrations of sorbitol and at whole temperature range has been perceived positive. The solute-solute interactions in the solutions of PEGs in sorbitol are manifested from the positive S_V^* values. But no regular trend has been obtained for S_V^* values which recommends the prevalence of solute-solvent interactions over solute-solute interactions. An irregular trend in S_V^* values indicates- solute-solute interactions being affected by some additional factors also [182].

Partial molar volume of transfer

At infinite dilution, the transfer volumes of PEGs from water to aqueous sorbitol solutions have been calculated from equation 4.3. The evaluated values of ΔV_{ϕ}^0 are indexed in Table

4.30. The positive ΔV_{ϕ}^0 values are observed for all PEGs and are rising with increase in concentration of sorbitol that deduces enormous desiccation results on PEGs. Relating to growing temperature, no steady trend has been detected in ΔV_{ϕ}^0 values. Regarding pure water's structure, the occurrence of an organizational grid of water along with comparatively big vacant areas – clathrates which can be infiltrated by diverse molecules, is presumed through the models defined by Pauling [183, 184]. Perhaps very insignificant amount of PEG molecules can be located in the crates of the water erections consequently not to eradicate the coop formation. Relatively larger content of PEGs abolishes a coop formation and as a result of formation of hydrogen bonds among water and organic molecules, newfangled structures are formed [170]. Moreover, the positive transfer volumes infer structure making/promoting ability of solutes as the structural moiety of sorbitol and PEG contains polar group.

Temperature dependent partial molar volume

By the means of general polynomial equation, the change in apparent molar volumes with temperature at infinite dilution can be uttered as equation 4.4. In aqueous sorbitol, the values of these constants for PEG-400 and PEG-4000 are reported in Table 4.31. These are utilized to analyze V_{ϕ}^0 and the deviations achieved from experimental and computed values are listed in Table 4.31. These deviations are evaluated by the means of equation 4.5. The values incorporated in Table 4.31 for deviations are very small that fits into the polynomial equation very magnificently which is manifested from R^2 values in the existing study.

The temperature dependence at infinite dilution of partial molar volume (V_{ϕ}^0) can be articulated in terms of absolute temperature (T) by the succeeding equation 4.6. The similar equation 4.6 is used to estimate partial molar expansibilities. At infinite dilution, the limiting apparent molar expansibility is well-thought-out to be a valuable measure [185] of solute-solvent interaction prevailing in liquid mixture. The general thermodynamic expression, given by Hepler [186] determined the structure breaking and making capability of solute in the solvent using equation 4.7. The structure breaking and making ability of solute in solvent can be decided [186, 187] via sign of $(\partial E_{\phi}^0/\partial T)_p$. The positive and

minute negative values of $(\partial E_{\phi}^0/\partial T)_p$ has been observed for the structure making solutes whereas negative values are detected for the solutes comprising structure breaking capacity. The values of partial molar expansibilities E_{ϕ}^0 and $(\partial E_{\phi}^0/\partial T)_p$ are ascribed in Table 4.32. The $E_{\phi}^0 = (\partial V_{\phi}^0/\partial T)_p$ values are found to be positive at entire concentrations of sorbitol and entire temperature range. The solute-solvent interactions are specified by the positive E_{ϕ}^0 values in the present ternary systems, as previously proposed by apparent molar volume statistics. Values of E_{ϕ}^0 show an asymmetrical trend with an upsurge in temperature as well as in concentration of sorbitol solutions. The small negative and positive $(\partial E_{\phi}^0/\partial T)_p$ values for mixtures of PEGs recommend the structure making ability of PEGs in whole aqueous sorbitol solutions.

Ultrasonic speed

The values of speed of sound, c for PEG-400 and PEG-4000 in (0.00, 0.01, 0.03, 0.05) mol·kg⁻¹ aqueous sorbitol solutions are determined at different temperatures ($T = 288.15$ - 318.15) K and are attributed in Table 4.33. The experimental ultrasonic speeds for (PEG-400 + water and PEG-4000 + water) have been compared with the literature values [118, 200] and are represented graphically in Figures 4.29 and 4.30. It is noticed from Table 4.33 that the values of speed of sound differ in order with respect to the temperature as well as the concentration of sorbitol. This increase in ultrasonic speed values relating to temperature is characteristic for water and is concerned with the 3-dimensional network of hydrogen bonds in the structure of water [170]. The increase in ultrasonic speed in any solution suggests the greater connotation midst the molecules of the solution. The greater connotation is due to intramolecular hydrogen bonding amongst solute molecules itself and intermolecular hydrogen bonds amid solute and solvent molecule [168]. Also, the speed of sound escalates with upsurge in the molality of PEGs for a specific concentration of the sorbitol, as the sorbitol molecules interrelate positively with water to support H-bond network in solvent [145]. Further, while the addition of PEG to the solvent, hydrogen bonds among sorbitol and water molecules get hampered and are demolished. Simultaneously,

new hydrogen bonds among molecules of solvent (sorbitol + water) and molecules of PEGs are designed [170].

Apparent molar isentropic compression

By the means of equation 4.8, apparent molar isentropic compression for PEGs in mixed aqueous and aqueous solutions of the sorbitol at different temperatures has been evaluated. An isentropic compressibility has been evaluated from equation 4.9. The calculated values of $K_{\phi,s}$ for several molal concentrations (m_A) of PEG-400 and PEG-4000 in aqueous sorbitol solutions at different temperatures are described in Table 4.33. From the evaluated values of $K_{\phi,s}$, it has been analyzed that values are negative for entire concentrations of the sorbitol and for whole temperature range. These $K_{\phi,s}$ values tend to be less negative with rise in the temperature and the concentration of the sorbitol due to progress of system at larger temperatures but increasing molality of PEGs results in the more negative $K_{\phi,s}$ values. The negative $K_{\phi,s}$ values specify that water molecules around the solute are not as much compressible as water molecules in bulk solution [188, 189] ensuing in the contraction of water molecules around it as of hydrophobic interactions of a non-polar group. Consequently, pressure on the bulk water molecules fallouts in the compressibility of solution, that additionally advocates the robust solute-solvent interactions among the molecules of PEGs and sorbitol's molecules.

Partial molar isentropic compression

The partial molar isentropic compression ($K_{\phi,s}^o$) can be premeditated through detecting change in apparent molar isentropic compression ($K_{\phi,s}$) along with molal concentration and is epitomized by equation 4.10. The S_K^* values along with the standard errors obtained by method of least squares fitting and $K_{\phi,s}^o$ values are reported in Table 4.34 and are represented in Figure 4.31. The lesser $K_{\phi,s}^o$ values for PEGs in aqueous sorbitol solutions at greater temperatures indicate the release of some water molecules to the bulk. The values of $K_{\phi,s}^o$ tend to be more negative at lower temperatures which points towards the strong

attractive interactions amongst PEGs and water molecules [191]. No systematic trend is observed for variation of $K_{\phi,s}^o$ with sorbitol concentration.

Partial molar isentropic compressions of transfer

For each PEG at infinite dilution, from water to aqueous sorbitol solutions, partial molar isentropic compressions of transfer ($\Delta K_{\phi,s}^o$) are evaluated from equation 4.11. The computed $\Delta K_{\phi,s}^o$ values are reported in Table 4.35. At all the sorbitol's concentrations, $\Delta K_{\phi,s}^o$ values are observed to be positive except for PEG-400 in (0.03 and 0.05) mol·kg⁻¹ aqueous sorbitol solutions and for PEG-4000 in 0.03 mol·kg⁻¹ aqueous sorbitol solutions at high temperature, $T = 318.15$ K. Thus, intimating the predominance of interactions among PEGs and sorbitol which further infers structure making tendency of ions.

Pair and triplet interaction coefficients

The pair and triplet interaction coefficients are computed based upon McMillan–Mayer theory [195] of liquid mixtures which allows the parting of effects because of interactions among the pairs of molecules of solute and those owing to its interaction among above two molecules of solute. This theory was then further being discussed by Friedman and Krishnan [196] and Franks *et al.* [197] to facilitate cosolute-solute interactions in solvation spheres. Therefore, partial molar volume of transfer (ΔV_{ϕ}^o) and the partial molar isentropic compression of transfer ($\Delta K_{\phi,s}^o$) can be articulated as equations 4.12 and 4.13. Pair and triplet coefficients are symbolized by corresponding parameters, for volume V_{AB} , V_{ABB} and for isentropic compression K_{AB} , K_{ABB} . Through fitting of ΔV_{ϕ}^o and $\Delta K_{\phi,s}^o$ values to equations 4.12 and 4.13, the values of V_{AB} , V_{ABB} , K_{AB} and K_{ABB} are computed and are detailed in Table 4.36. Pair interaction coefficients V_{AB} and K_{AB} are positive at all temperatures for both PEGs except for V_{AB} values of PEG-400. The triplet interaction coefficient for volume V_{ABB} is negative for PEG-400 at all temperatures except at lower temperature 288.15 K and positive for PEG-4000 at entire temperature range. Also, the triplet interaction coefficient for isentropic compression K_{ABB} is negative for both PEGs at whole temperatures except

for PEG-400 at 308.15 K. Overall positive values for pair interaction coefficients V_{AB} and K_{AB} infers [198, 199] the dominance of pair-wise interactions in the present ternary systems of PEGs-sorbitol-water.

Table 4.28

Values of densities, ρ , and apparent molar volumes, V_ϕ of PEGs in aqueous solutions of sorbitol at different temperatures and experimental pressure, $p = 0.1$ MPa.

$^a m_A$ (mol·kg ⁻¹)	$\rho \times 10^{-3}$ (kg·m ⁻³)				$V_\phi \times 10^6$ (m ³ ·mol ⁻¹)			
	T= 288.15 K	T= 298.15 K	T= 308.15 K	T= 318.15 K	T= 288.15 K	T= 298.15 K	T= 308.15 K	T= 318.15 K
<i>PEG-400 + 0.00m Sorbitol</i>								
0.00000	0.999257	0.997047	0.994039	0.990356				
0.00498	0.999615	0.997395	0.994377	0.990687	328.28	330.74	333.61	336.11
0.01000	0.999968	0.997739	0.994709	0.991011	328.89	331.37	334.34	336.93
0.01499	1.000311	0.998072	0.995030	0.991323	329.51	332.08	335.15	337.78
0.01992	1.000643	0.998393	0.995339	0.991624	330.16	332.78	335.91	338.56
0.02453	1.000946	0.998687	0.995621	0.991898	330.78	333.39	336.58	339.27
0.03006	1.001301	0.999027	0.995949	0.992218	331.51	334.26	337.45	340.09
0.03525	1.001626	0.999340	0.996249	0.992512	332.21	334.97	338.21	340.79
0.03992	1.001908	0.999614	0.996511	0.992768	332.91	335.65	338.89	341.46
<i>PEG-400 + 0.01m Sorbitol</i>								
0.00000	0.999887	0.997823	0.994845	0.990914				
0.00513	1.000245	0.998173	0.995186	0.991243	330.11	332.26	334.89	338.25
0.01011	1.000584	0.998504	0.995508	0.991556	330.81	333.02	335.55	338.74
0.01508	1.000915	0.998826	0.995822	0.991860	331.52	333.76	336.29	339.45

0.02036	1.001258	0.999159	0.996148	0.992175	332.26	334.52	336.98	340.18
0.02516	1.001560	0.999455	0.996437	0.992452	332.97	335.17	337.62	340.89
0.03029	1.001875	0.999762	0.996738	0.992741	333.73	335.91	338.29	341.62
0.03479	1.002144	1.000027	0.996994	0.992990	334.39	336.51	338.92	342.18
0.03898	1.002389	1.000268	0.997233	0.993217	335.01	337.05	339.37	342.69
<i>PEG-400 + 0.03m Sorbitol</i>								
0.00000	1.001172	0.999084	0.996047	0.992106				
0.00521	1.001523	0.999428	0.996385	0.992433	332.27	334.09	336.08	339.37
0.01056	1.001877	0.999775	0.996726	0.992761	332.68	334.55	336.52	339.91
0.01501	1.002167	1.000059	0.997005	0.993030	333.05	334.94	336.96	340.35
0.02009	1.002494	1.000378	0.997317	0.993330	333.46	335.41	337.45	340.88
0.02540	1.002828	1.000705	0.997637	0.993638	333.95	335.89	337.95	341.37
0.02999	1.003112	1.000983	0.997907	0.993897	334.35	336.29	338.43	341.88
0.03531	1.003436	1.001300	0.998214	0.994193	334.81	336.75	338.99	342.41
0.04001	1.003718	1.001576	0.998479	0.994447	335.19	337.12	339.48	342.93
<i>PEG-400 + 0.05m Sorbitol</i>								
0.00000	1.002435	1.000322	0.997257	0.993322				
0.00542	1.002796	1.000667	0.997594	0.993645	332.61	336.22	338.51	342.18
0.01005	1.003101	1.000956	0.997877	0.993917	332.95	336.58	338.89	342.52
0.01500	1.003421	1.001261	0.998174	0.994200	333.31	336.98	339.34	343.05

0.02006	1.003744	1.001568	0.998471	0.994485	333.72	337.38	339.82	343.55
0.02497	1.004051	1.001860	0.998756	0.994754	334.11	337.78	340.24	344.06
0.02948	1.004328	1.002125	0.999011	0.994998	334.51	338.13	340.68	344.49
0.03491	1.004654	1.002439	0.999311	0.995284	335.02	338.55	341.23	345.04
0.03985	1.004947	1.002720	0.999579	0.995540	335.46	338.93	341.71	345.52
<i>PEG-4000 + 0.00m Sorbitol</i>								
0.00000	0.999257	0.997047	0.994039	0.990356				
0.00501	1.002520	1.000329	0.997349	0.993702	3339.71	3341.92	3344.25	3346.63
0.01003	1.005677	1.003504	1.000552	0.996942	3340.48	3342.64	3344.86	3347.26
0.01504	1.008720	1.006567	1.003643	1.000068	3341.19	3343.21	3345.41	3347.71
0.02001	1.011640	1.009503	1.006610	1.003066	3341.82	3343.89	3345.9	3348.39
0.02496	1.014452	1.012333	1.009465	1.005955	3342.48	3344.51	3346.61	3349.02
0.02929	1.016838	1.014735	1.011886	1.008405	3343.02	3345.02	3347.23	3349.63
0.03503	1.019898	1.017820	1.015002	1.011553	3343.79	3345.61	3347.76	3350.29
0.03994	1.022434	1.020372	1.017576	1.014160	3344.26	3346.11	3348.32	3350.75
<i>PEG-4000 + 0.01m Sorbitol</i>								
0.00000	0.999887	0.997823	0.994845	0.990914				
0.00491	1.003069	1.001024	0.998072	0.994179	3341.58	3343.21	3345.75	3348.39
0.01011	1.006322	1.004297	1.001374	0.997519	3342.25	3343.89	3346.25	3349.01
0.01499	1.009271	1.007265	1.004366	1.000548	3342.89	3344.41	3346.91	3349.57

0.02008	1.012246	1.010254	1.007385	1.003609	3343.51	3345.25	3347.54	3349.91
0.02538	1.015237	1.013264	1.010425	1.006685	3344.17	3345.91	3348.06	3350.49
0.02988	1.017698	1.015735	1.012920	1.009217	3344.64	3346.58	3348.68	3350.96
0.03476	1.020289	1.018340	1.015546	1.011879	3345.12	3347.07	3349.32	3351.53
0.04008	1.023024	1.021086	1.018321	1.014692	3345.63	3347.72	3349.86	3352.04
<i>PEG-4000 + 0.03m Sorbitol</i>								
0.00000	1.001172	0.999084	0.996047	0.992106				
0.00518	1.004502	1.002431	0.999418	0.995515	3342.86	3345.13	3348.52	3351.67
0.01003	1.007513	1.005457	1.002467	0.998598	3343.41	3345.76	3349.11	3352.26
0.01508	1.010540	1.008504	1.005536	1.001704	3344.26	3346.29	3349.74	3352.74
0.01999	1.013386	1.011368	1.008421	1.004625	3344.91	3346.89	3350.32	3353.25
0.02499	1.016191	1.014190	1.011263	1.007503	3345.53	3347.46	3350.97	3353.81
0.03009	1.018963	1.016976	1.014067	1.010341	3345.98	3347.99	3351.59	3354.49
0.03492	1.021503	1.019528	1.016638	1.012945	3346.49	3348.61	3352.21	3355.06
0.03965	1.023919	1.021950	1.019078	1.015416	3346.91	3349.25	3352.88	3355.69
<i>PEG-4000 + 0.05m Sorbitol</i>								
0.00000	1.002435	1.000322	0.997257	0.993322				
0.00498	1.005615	1.003517	1.000473	0.996575	3344.19	3346.88	3350.85	3353.79
0.01005	1.008741	1.006658	1.003635	0.999775	3344.86	3347.51	3351.46	3354.37
0.01523	1.011823	1.009757	1.006756	1.002932	3345.51	3348.03	3351.92	3354.95

0.01997	1.014551	1.012499	1.009515	1.005724	3346.05	3348.59	3352.58	3355.61
0.02486	1.017275	1.015240	1.012274	1.008513	3346.68	3349.08	3353.11	3356.27
0.03011	1.020106	1.018087	1.015139	1.011412	3347.24	3349.61	3353.69	3356.85
0.03502	1.022762	1.020661	1.017734	1.014037	3347.96	3350.18	3354.18	3357.38
0.04010	1.025423	1.023240	1.020341	1.016666	3348.64	3350.79	3354.53	3357.99

^a m_A is the molality of PEGs in aqueous sorbitol solutions; Standard uncertainties u are $u(m) = 2 \times 10^{-5} \text{ mol} \cdot \text{kg}^{-1}$, $u(T) = 0.01 \text{ K}$, $u(\rho) = 0.05 \text{ kg} \cdot \text{m}^{-3}$ and $u(p) = 0.01 \text{ MPa}$.

Table 4.29

Limiting apparent molar volumes, V_{ϕ}° , and experimental slopes, S_V^* of PEGs in aqueous solutions of sorbitol at different temperatures.

${}^a m_B$	$V_{\phi}^{\circ} \times 10^6 \text{ (m}^3 \cdot \text{mol}^{-1}\text{)}$					$S_V^* \times 10^6 \text{ (m}^3 \cdot \text{kg} \cdot \text{mol}^{-2}\text{)}$				
	$T=288.15 \text{ K}$	$T=298.15 \text{ K}$	$T=308.15 \text{ K}$	$T=318.15 \text{ K}$	$T=308.15 \text{ K}$	$T=288.15 \text{ K}$	$T=298.15 \text{ K}$	$T=308.15 \text{ K}$	$T=318.15 \text{ K}$	$T=318.15 \text{ K}$
PEG-400										
0.00	327.56(±0.04)	329.98(±0.03)	332.86(±0.02)	335.44(±0.06)	335.44(±0.06)	132.24(±1.40)	141.54(±1.21)	151.85(±0.80)	153.02(±2.37)	153.02(±2.37)
0.01	329.34(±0.02)	331.59(±0.04)	334.23(±0.04)	337.46(±0.05)	337.46(±0.05)	144.91(±0.64)	141.47(±1.38)	133.60(±1.39)	135.15(±2.12)	135.15(±2.12)
0.03	331.79(±0.02)	333.63(±0.02)	335.50(±0.02)	338.83(±0.03)	338.83(±0.03)	84.96(±0.76)	87.98(±0.63)	98.31(±1.32)	101.76(±0.71)	101.76(±0.71)
0.05	332.10(±0.04)	335.79(±0.01)	337.96(±0.03)	341.58(±0.02)	341.58(±0.02)	82.93(±1.59)	78.97(±0.27)	93.19(±1.07)	98.68(±1.11)	98.68(±1.11)
PEG-4000										
0.00	3339.16(±0.06)	3341.42(±0.07)	3343.65(±0.06)	3346.00(±0.06)	3346.00(±0.06)	130.74(±2.49)	120.34(±2.61)	117.74(±2.24)	120.70(±2.29)	120.70(±2.29)
0.01	3341.11(±0.07)	3342.57(±0.06)	3345.12(±0.05)	3347.93(±0.05)	3347.93(±0.05)	115.94(±2.89)	130.28(±2.45)	119.04(±1.77)	102.27(±1.98)	102.27(±1.98)
0.03	3342.36(±0.12)	3344.54(±0.04)	3347.84(±0.03)	3351.03(±0.06)	3351.03(±0.06)	119.17(±4.82)	117.25(±1.45)	125.58(±1.04)	115.31(±2.33)	115.31(±2.33)
0.05	3343.58(±0.04)	3346.37(±0.03)	3350.37(±0.07)	3353.18(±0.04)	3353.18(±0.04)	124.87(±1.53)	109.35(±1.17)	107.53(±2.84)	120.88(±1.62)	120.88(±1.62)

^a m_B is the molality of aqueous solutions of sorbitol.

Table 4.30

Partial molar volume of transfer, ΔV_{ϕ}^o of PEGs in aqueous solutions of sorbitol at different temperatures.

${}^a m_B$ (mol·kg ⁻¹)	$\Delta V_{\phi}^o \times 10^6$ (m ³ ·mol ⁻¹)			
	$T= 288.15$ K	$T= 298.15$ K	$T= 308.15$ K	$T= 318.15$ K
PEG-400				
0.01	1.78	1.62	1.38	2.02
0.03	4.23	3.66	2.64	3.39
0.05	4.54	5.82	5.10	6.15
PEG-4000				
0.01	1.95	1.15	1.46	1.93
0.03	3.20	3.12	4.19	5.02
0.05	4.41	4.95	6.71	7.17

^a m_B is the molality of aqueous solutions of sorbitol.

Table 4.31

Values of empirical parameters of equation 4.4 for PEGs in aqueous sorbitol solutions.

${}^a m_B$ (mol·kg ⁻¹)	$A \times 10^6$ (m ³ ·mol ⁻¹)	$B \times 10^6$ (m ³ ·mol ⁻¹ ·K ⁻¹)	$C \times 10^6$ (m ³ ·mol ⁻¹ ·K ⁻²)	R^2	ARD
PEG-400					
0.00	330.09	0.261	0.0004	0.9999	0.00023
0.01	335.35	0.308	-0.0002	0.9999	0.01110
0.03	333.42	0.193	0.0037	0.9999	0.00043
0.05	331.56	0.246	0.0024	0.9999	0.01098
0.07	330.09	0.261	0.0004	0.9999	0.00023
PEG-4000					
0.00	3341.40	0.225	0.0002	0.9999	0.00000
0.01	3342.69	0.196	0.0034	0.9999	0.00002
0.03	3344.72	0.268	0.0025	0.9999	0.00004
0.05	3346.73	0.328	0.0001	0.9999	0.00007

^a m_B is the molality of aqueous solutions of sorbitol.

Table 4.32

Limiting apparent molar expansibilities, E_{ϕ}^0 for PEGs in aqueous sorbitol solutions at different temperatures.

${}^a m_B$ (mol·kg ⁻¹)	$E_{\phi}^0 \times 10^6$ (m ³ ·mol ⁻¹ ·K ⁻¹)				$(\partial E_{\phi}^0 / \partial T)_p$ (m ³ ·mol ⁻¹ ·K ⁻²)
	$T= 288.15$ K	$T= 298.15$ K	$T= 308.15$ K	$T= 318.15$ K	
PEG-400					
0.00	0.2527	0.2610	0.2692	0.2774	0.0008
0.01	0.3115	0.3080	0.3045	0.3009	-0.0004
0.03	0.1555	0.1926	0.2298	0.2669	0.0074
0.05	0.1969	0.2456	0.2943	0.3430	0.0049
PEG-4000					
0.00	0.2202	0.2252	0.2301	0.2350	0.0005
0.01	0.1280	0.1961	0.2641	0.3322	0.0068
0.03	0.2424	0.2677	0.2930	0.3183	0.0051
0.05	0.3266	0.3275	0.3284	0.3293	0.0001

${}^a m_B$ is the molality of aqueous solutions of sorbitol.

Table 4.33

Values of speed of sound, c , and apparent molar isentropic compression, $K_{\phi,s}$ of PEGs in aqueous solutions of sorbitol at different temperatures and experimental pressure, $p = 0.1$ MPa.

$^a m_A$ (mol·kg ⁻¹)	c (m·s ⁻¹)								$K_{\phi,s} \times 10^6$ (m ³ ·mol ⁻¹ ·GPa ⁻¹)			
	$T=288.15$ K	$T=298.15$ K	$T=308.15$ K	$T=318.15$ K	$T=288.15$ K	$T=298.15$ K	$T=308.15$ K	$T=318.15$ K	$T=288.15$ K	$T=298.15$ K	$T=308.15$ K	$T=318.15$ K
<i>PEG-400 + 0.00m Sorbitol</i>												
0.00000	1466.59	1495.85	1519.14	1536.02								
0.00498	1467.80	1497.03	1520.18	1537.09	-37.18	-35.70	-34.56	-33.74				
0.01000	1469.00	1498.22	1521.23	1538.17	-41.89	-40.25	-38.99	-38.11				
0.01499	1470.20	1499.40	1522.28	1539.25	-43.46	-41.76	-40.47	-39.56				
0.01992	1471.38	1500.57	1523.31	1540.32	-44.24	-42.52	-41.20	-40.29				
0.02453	1472.48	1501.67	1524.27	1541.32	-44.69	-42.95	-41.63	-40.71				
0.03006	1473.80	1502.98	1525.43	1542.52	-45.06	-43.30	-41.97	-41.04				
0.03525	1475.04	1504.21	1526.51	1543.64	-45.30	-43.54	-42.20	-41.27				
0.03992	1476.16	1505.32	1527.49	1544.65	-45.47	-43.70	-42.36	-41.42				
<i>PEG-400 + 0.01m Sorbitol</i>												
0.00000	1467.84	1497.55	1520.61	1537.24								
0.00513	1469.06	1498.77	1521.68	1538.35	-37.40	-35.90	-34.76	-33.95				
0.01011	1470.25	1499.95	1522.72	1539.43	-41.88	-40.21	-38.97	-38.10				

0.01508	1471.43	1501.12	1523.76	1540.50	-43.40	-41.69	-40.41	-39.52
0.02036	1472.69	1502.37	1524.86	1541.65	-44.22	-42.47	-41.18	-40.27
0.02516	1473.83	1503.51	1525.87	1542.68	-44.67	-42.90	-41.60	-40.69
0.03029	1475.05	1504.73	1526.94	1543.79	-44.99	-43.22	-41.90	-40.99
0.03479	1476.13	1505.79	1527.88	1544.77	-45.20	-43.42	-42.10	-41.18
0.03898	1477.12	1506.79	1528.76	1545.67	-45.36	-43.57	-42.25	-41.33
<i>PEG-400 + 0.03m Sorbitol</i>								
0.00000	1469.89	1499.13	1522.05	1538.75				
0.00521	1471.14	1500.37	1523.12	1539.88	-37.46	-35.98	-34.85	-34.03
0.01056	1472.42	1501.65	1524.24	1541.03	-41.97	-40.33	-39.09	-38.22
0.01501	1473.49	1502.71	1525.18	1541.99	-43.27	-41.59	-40.33	-39.43
0.02009	1474.70	1503.92	1526.24	1543.09	-44.07	-42.35	-41.07	-40.17
0.02540	1475.98	1505.19	1527.35	1544.24	-44.56	-42.83	-41.54	-40.63
0.02999	1477.07	1506.28	1528.31	1545.23	-44.85	-43.11	-41.81	-40.90
0.03531	1478.35	1507.55	1529.43	1546.38	-45.10	-43.35	-42.04	-41.12
0.04001	1479.48	1508.67	1530.41	1547.39	-45.27	-43.51	-42.20	-41.28
<i>PEG-400 + 0.05m Sorbitol</i>								
0.00000	1472.54	1501.21	1523.28	1540.42				
0.00542	1473.83	1502.50	1524.34	1541.60	-37.69	-36.23	-35.13	-34.29
0.01005	1474.93	1503.59	1525.31	1542.61	-41.60	-40.01	-38.83	-37.94
0.01500	1476.11	1504.77	1526.35	1543.68	-43.12	-41.48	-40.26	-39.35

0.02006	1477.32	1505.97	1527.41	1544.78	-43.91	-42.24	-41.01	-40.08
0.02497	1478.49	1507.14	1528.44	1545.85	-44.37	-42.68	-41.44	-40.51
0.02948	1479.56	1508.21	1529.38	1546.83	-44.67	-42.97	-41.72	-40.78
0.03491	1480.86	1509.49	1530.52	1548.01	-44.93	-43.22	-41.96	-41.02
0.03985	1482.03	1510.67	1531.55	1549.08	-45.10	-43.39	-42.13	-41.18
<i>PEG-4000 + 0.00m Sorbitol</i>								
0.00000	1466.59	1495.85	1519.14	1536.02				
0.00501	1476.52	1505.52	1529.06	1545.61	-37.53	-36.04	-34.89	-34.07
0.01003	1486.47	1515.48	1539.01	1555.56	-42.33	-40.67	-39.41	-38.52
0.01504	1496.39	1525.41	1548.93	1565.50	-44.01	-42.30	-41.00	-40.09
0.02001	1506.24	1535.26	1558.78	1575.35	-44.92	-43.17	-41.85	-40.93
0.02496	1516.05	1545.08	1568.58	1585.16	-45.51	-43.74	-42.41	-41.48
0.02929	1524.63	1553.66	1577.16	1593.75	-45.89	-44.11	-42.77	-41.83
0.03503	1536.01	1565.04	1588.53	1605.13	-46.29	-44.50	-43.15	-42.21
0.03994	1545.74	1574.78	1598.26	1614.86	-46.57	-44.77	-43.41	-42.47
<i>PEG-4000 + 0.01m Sorbitol</i>								
0.00000	1467.84	1497.55	1520.61	1537.24				
0.00491	1477.63	1507.42	1530.92	1546.67	-37.29	-35.79	-34.66	-33.84
0.01011	1487.94	1517.73	1541.23	1556.97	-42.30	-40.62	-39.38	-38.50
0.01499	1497.62	1527.41	1550.90	1566.64	-43.93	-42.19	-40.91	-40.01
0.02008	1507.71	1537.50	1560.98	1576.72	-44.85	-43.08	-41.78	-40.87

0.02538	1518.22	1548.01	1571.49	1587.22	-45.47	-43.68	-42.36	-41.45
0.02988	1527.15	1556.94	1580.40	1596.13	-45.85	-44.05	-42.73	-41.81
0.03476	1536.82	1566.61	1590.08	1605.79	-46.19	-44.38	-43.04	-42.12
0.04008	1547.38	1577.17	1600.62	1616.33	-46.49	-44.67	-43.33	-42.40
<i>PEG-4000 + 0.03m Sorbitol</i>								
0.00000	1469.89	1499.13	1522.05	1538.75				
0.00518	1480.16	1509.47	1532.75	1548.94	-37.70	-36.21	-35.09	-34.26
0.01003	1489.77	1519.07	1542.35	1558.54	-42.15	-40.51	-39.27	-38.39
0.01508	1499.76	1529.07	1552.35	1568.54	-43.83	-42.13	-40.86	-39.96
0.01999	1509.48	1538.79	1562.08	1578.26	-44.71	-42.98	-41.69	-40.78
0.02499	1519.38	1548.69	1571.98	1588.15	-45.30	-43.55	-42.24	-41.33
0.03009	1529.48	1558.79	1582.08	1598.25	-45.74	-43.97	-42.66	-41.74
0.03492	1539.04	1568.35	1591.64	1607.81	-46.07	-44.29	-42.96	-42.04
0.03965	1548.40	1577.72	1601.01	1617.17	-46.33	-44.54	-43.22	-42.29
<i>PEG-4000 + 0.05m Sorbitol</i>								
0.00000	1472.54	1501.21	1523.28	1540.42				
0.00498	1482.29	1511.10	1533.33	1550.34	-37.23	-35.78	-34.70	-33.87
0.01005	1492.32	1521.14	1543.36	1560.37	-42.02	-40.41	-39.22	-38.33
0.01523	1502.58	1531.39	1553.60	1570.62	-43.71	-42.05	-40.82	-39.90
0.01997	1511.96	1540.76	1562.98	1580.00	-44.55	-42.86	-41.61	-40.69
0.02486	1521.64	1550.44	1572.65	1589.68	-45.12	-43.41	-42.16	-41.22

0.03011	1532.03	1560.83	1583.03	1600.07	-45.57	-43.85	-42.58	-41.64
0.03502	1541.75	1570.54	1592.74	1609.79	-45.90	-44.16	-42.89	-41.95
0.04010	1551.80	1580.59	1602.79	1619.84	-46.19	-44.44	-43.16	-42.21

^a m_A is the molality of PEGs in aqueous sorbitol solutions; Standard uncertainties u are $u(m) = 2 \times 10^{-5} \text{ mol} \cdot \text{kg}^{-1}$, $u(T) = 0.01 \text{ K}$, $u(c) = 0.5 \text{ m} \cdot \text{s}^{-1}$ and $u(p) = 0.01 \text{ MPa}$.

Table 4.34

Limiting apparent molar isentropic compression, $K_{\phi,s}^o$ and experimental slope, S_K^* for PEGs in aqueous solutions of sorbitol at different temperatures.

${}^a m_B$ (mol·kg ⁻¹)	$K_{\phi,s}^o \times 10^6$ (m ³ ·mol ⁻¹ ·GPa ⁻¹)				$S_K^* \times 10^6$ (kg·m ³ ·mol ⁻² ·GPa ⁻¹)			
	T= 288.15 K	T= 298.15 K	T= 308.15 K	T= 318.15 K	T= 288.15 K	T= 298.15 K	T= 308.15 K	T= 318.15 K
PEG-400								
0.00	-39.13(±1.26)	-37.59(±1.22)	-36.40(±1.19)	-35.55(±1.17)	-190.51(±49.92)	-183.84(±48.20)	-179.21(±47.02)	-176.53(±46.33)
0.01	-39.11(±1.20)	-37.54(±1.16)	-36.37(±1.13)	-35.53(±1.11)	-190.55(±47.68)	-183.75(±45.99)	-179.22(±44.87)	-176.65(±44.26)
0.03	-39.21(±1.18)	-37.66(±1.14)	-36.50(±1.12)	-35.66(±1.10)	-181.16(±46.64)	-174.82(±45.02)	-170.57(±43.95)	-168.10(±43.34)
0.05	-39.20(±1.10)	-37.68(±1.06)	-36.56(±1.04)	-35.70(±1.02)	-177.10(±43.60)	-170.99(±42.12)	-167.02(±41.17)	-164.48(±40.58)
PEG-4000								
0.00	-39.34(±1.26)	-37.78(±1.22)	-36.59(±1.19)	-35.74(±1.17)	-213.82(±50.06)	-206.63(±48.35)	-201.66(±47.14)	-198.98(±46.48)
0.01	-39.18(±1.29)	-37.61(±1.24)	-36.44(±1.21)	-35.60(±1.20)	-215.91(±51.08)	-208.36(±49.28)	-203.36(±48.05)	-200.99(±47.44)
0.03	-39.31(±1.18)	-37.76(±1.14)	-36.60(±1.11)	-35.75(±1.10)	-207.60(±47.00)	-200.50(±45.37)	-195.72(±44.26)	-193.33(±43.68)
0.05	-39.04(±1.25)	-37.54(±1.21)	-36.42(±1.18)	-35.56(±1.17)	-210.39(±49.49)	-203.14(±47.86)	-198.58(±46.76)	-195.93(±46.10)

^a m_B is the molality of aqueous solutions of sorbitol.

Table 4.35

Partial molar isentropic compression of transfer, $\Delta K_{\phi,s}^o$ of PEGs in aqueous solutions of sorbitol at different temperatures.

${}^a m_B (\text{mol} \cdot \text{kg}^{-1})$	$\Delta K_{\phi,s}^o \times 10^6 (\text{m}^3 \cdot \text{mol}^{-1} \cdot \text{GPa}^{-1})$			
	$T= 288.15 \text{ K}$	$T= 298.15 \text{ K}$	$T= 308.15 \text{ K}$	$T= 318.15 \text{ K}$
PEG-400				
0.01	0.03	0.05	0.03	0.02
0.03	-0.07	-0.08	-0.10	-0.10
0.05	-0.06	-0.10	-0.16	-0.15
PEG-4000				
0.01	0.16	0.17	0.15	0.14
0.03	0.03	0.02	0.00	-0.01
0.05	0.29	0.24	0.17	0.18

${}^a m_B$ is the molality of aqueous solutions of sorbitol.

Table 4.36

Pair and triplet interaction coefficients of PEGs in aqueous solutions of sorbitol at different temperatures.

T (K)	$V_{AB} \times 10^6$ ($\text{m}^3 \cdot \text{mol}^{-2} \cdot \text{kg}$)	$V_{ABB} \times 10^6$ ($\text{m}^3 \cdot \text{mol}^{-3} \cdot \text{kg}^2$)	$K_{AB} \times 10^6$ ($\text{m}^3 \cdot \text{mol}^{-2} \cdot \text{kg} \cdot \text{GPa}^{-1}$)	$K_{ABB} \times 10^6$ ($\text{m}^3 \cdot \text{mol}^{-3} \cdot \text{kg}^2 \cdot \text{GPa}^{-1}$)
PEG-400				
288.15	-0.78	1.12	105.45	-798.74
298.15	-0.14	-12.50	72.18	-192.86
308.15	-0.31	-18.21	46.80	44.82
318.15	-0.84	-9.34	69.64	-126.83
PEG-4000				
288.15	0.82	24.94	81.61	-512.25
298.15	1.32	10.76	57.02	-101.13
308.15	1.05	5.61	74.10	-93.19
318.15	0.66	11.68	102.03	-404.42

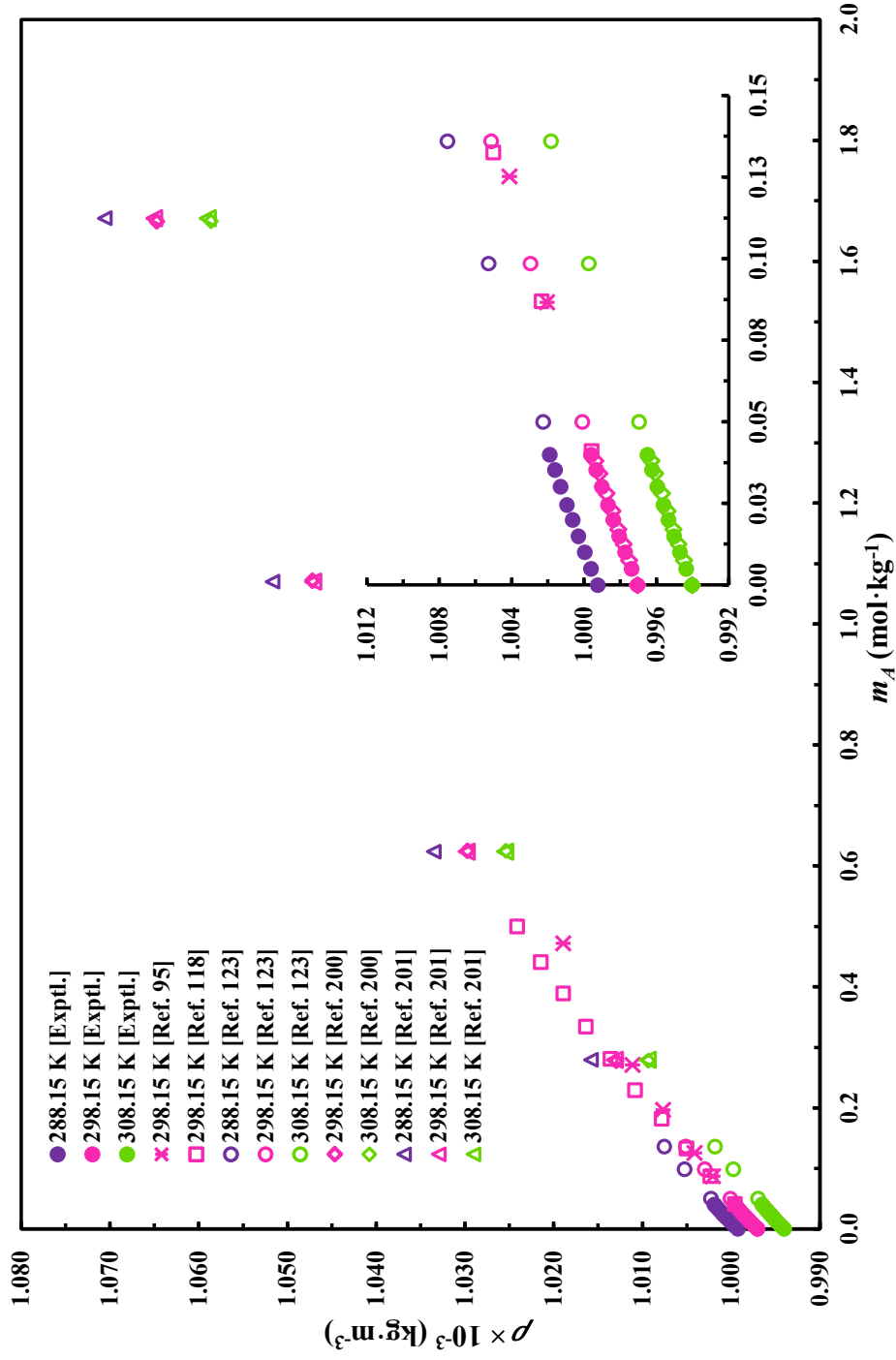


Figure 4.26: Plots of experimental and literature values [95, 118, 123, 200, 201] of densities for (PEG-400 + water) mixtures at different temperatures.

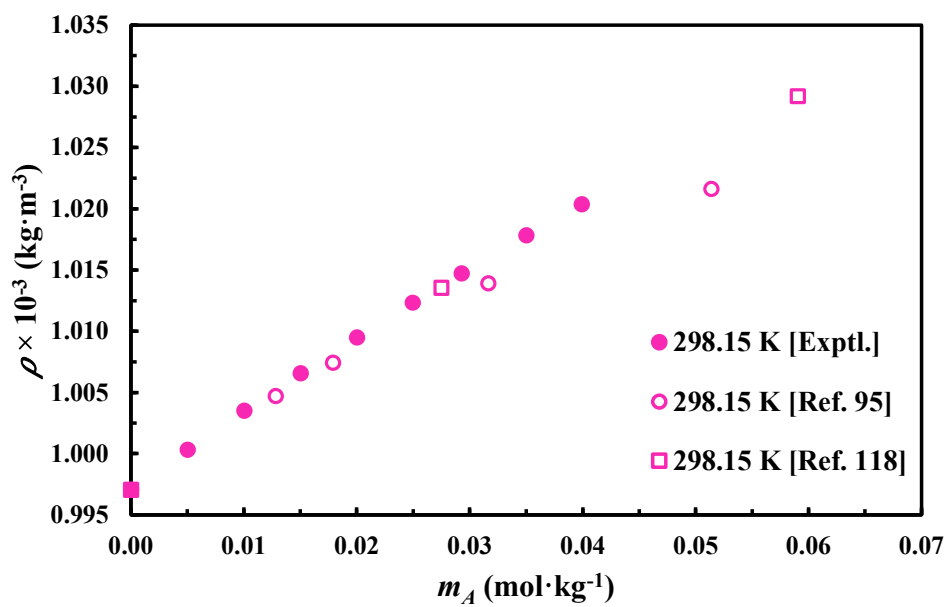


Figure 4.27: Plots of experimental and literature values [95, 118] of densities for (PEG-4000 + water) mixtures at temperature 298.15 K.

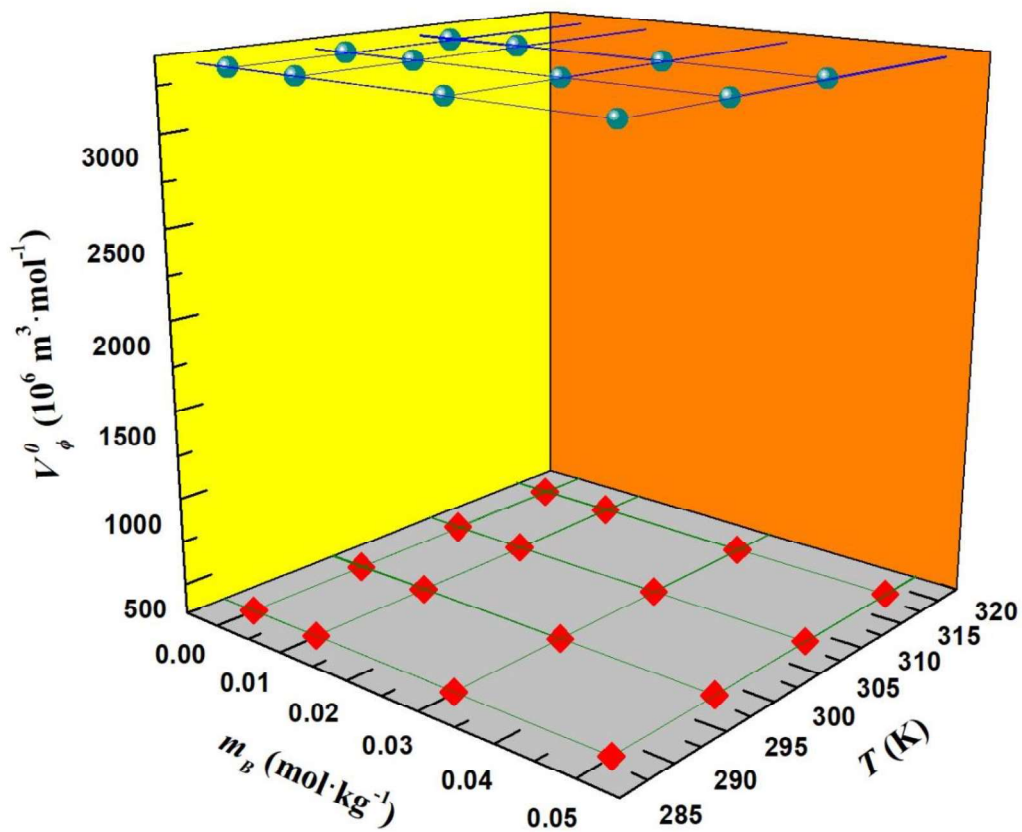


Figure 4.28: Plots of partial molar volume V_ϕ^o for PEG-400 (\blacklozenge) and PEG-4000 (\bullet) in different concentrations of aqueous sorbitol solutions at different temperatures.

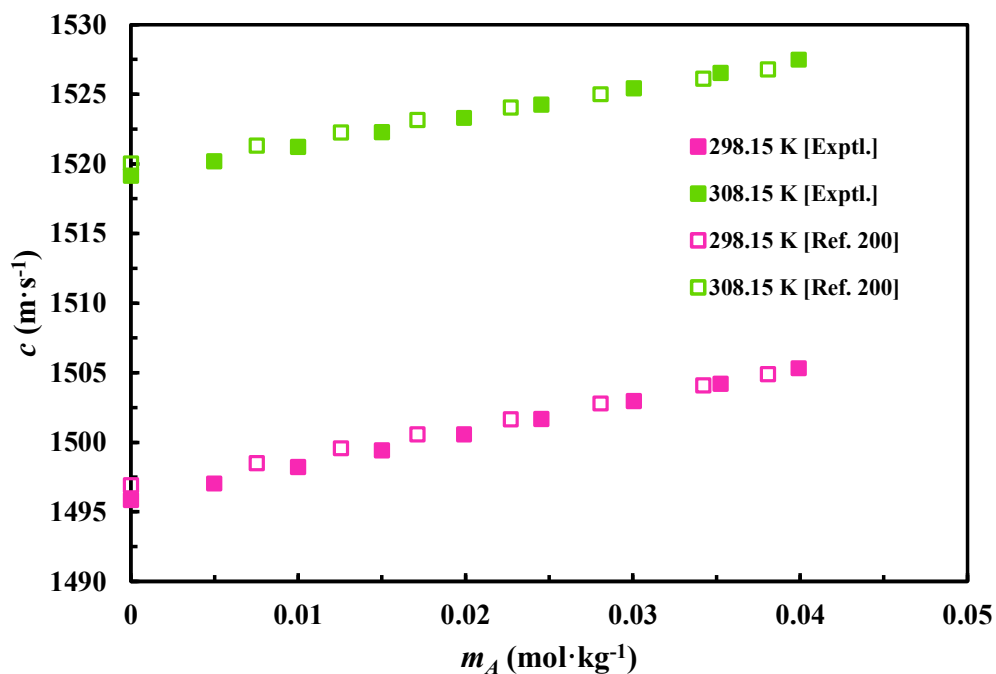


Figure 4.29: Plots of experimental and literature values [200] of ultrasonic speeds for (PEG-400 + water) mixtures at different temperatures.

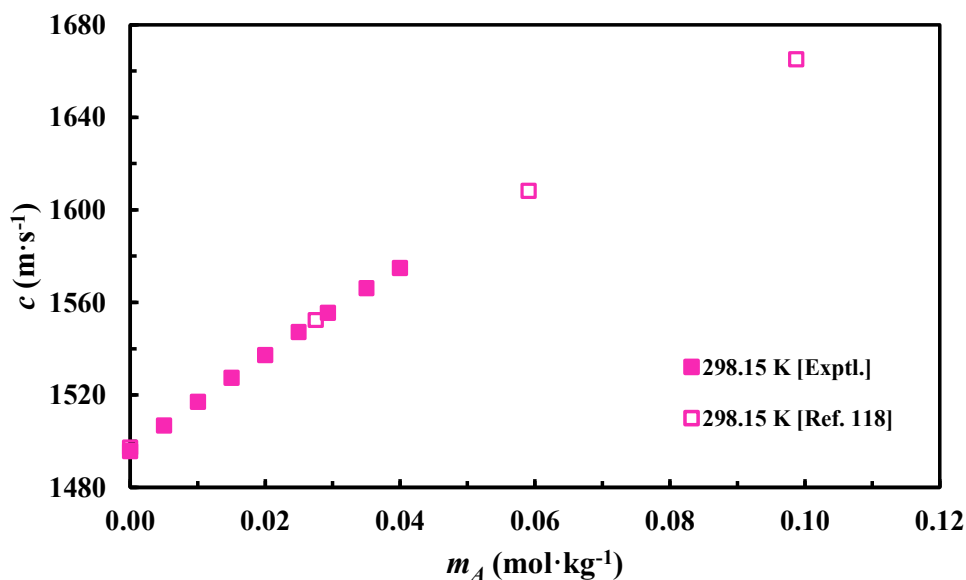


Figure 4.30: Plots of experimental and literature values [118] of ultrasonic speeds for (PEG-4000 + water) mixtures at temperature 298.15 K.

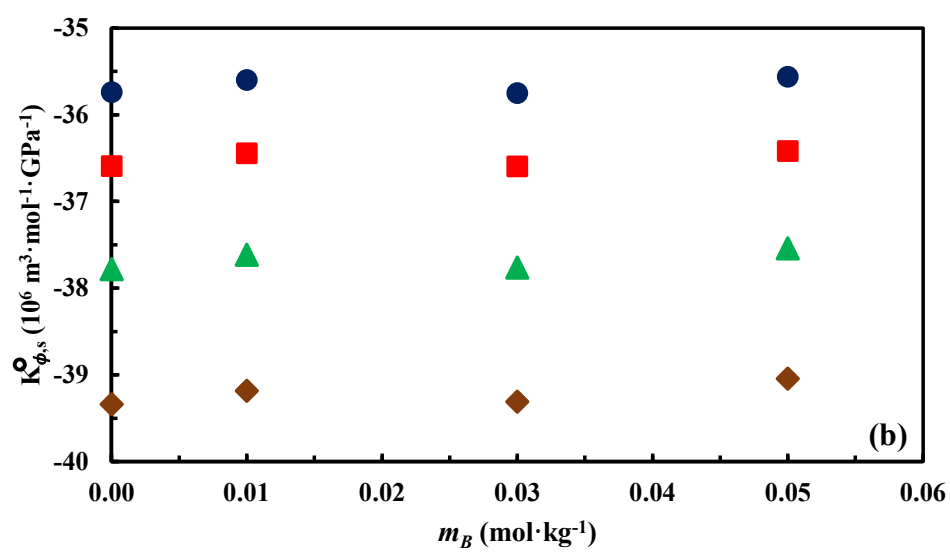
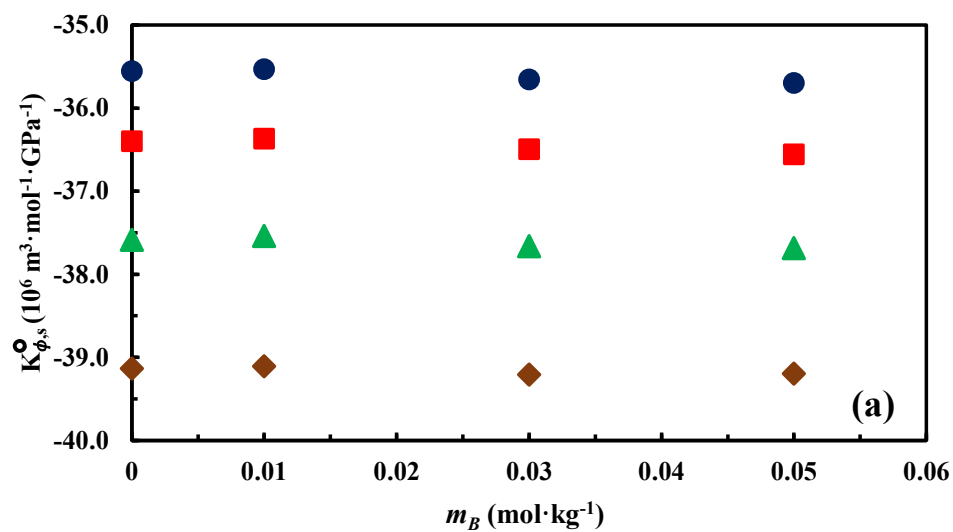


Figure 4.31: Plots of partial molar isentropic compression $K_{\phi,s}^o$ for (a) PEG-400 (b) PEG-4000 at temperatures (◆, 288.15 K; ▲, 298.15 K; ■, 308.15 K; ●, 318.15 K) in different concentrations of aqueous sorbitol solutions.

Section V

In this section, we have reported the thermodynamic and acoustical properties for binary systems (EG + Glycerol, DEG + Glycerol, TEG + Glycerol). The values for acoustic impedance and adiabatic compressibility for all three binary systems is enlisted in Table 4.37. Intermolecular free lengths and attenuation coefficients are attributed in Table 4.38, Relaxation times and free volumes in Table 4.39, Molar volumes and available volumes in Table 4.40, Wada's Constants and Rao's Constants Table 4.41, Vander Waal's constants and Gibb's Free Energy in Table 4.42, values for internal pressure and Enthalpies are incorporated in Table 4.43. The plots for all thermodynamic parameters are shown in Figures 4.32 to 4.43. We have also computed excess molar volume and excess Gibb's free energy of activation and the values obtained are enlisted in Table 4.44 and are plotted in Figures 4.44 to 4.46. By using theoretical models given by Nomoto, Jungie, Van Dael and Vangeel, and impedance relation, we have calculated theoretical ultrasonic speeds and are attributed in Table 4.45 and Table 4.46. The percentage deviations of experimental values from theoretical models have also been evaluated and is given in Table 4.47 and Table 4.48.

ACOUSTIC IMPEDANCE (Z), ADIABATIC COMPRESSIBILITY (β), INTERMOLECULAR FREE LENGTH (L_f)

From figures, it can be noticed that acoustic impedance for the binary systems (EG + Glycerol, DEG + Glycerol, TEG + Glycerol) is decreasing with increase in mole fraction of EGs. The reduction in values of Z has also been observed with respect to temperature. Further, the adiabatic compressibility and intermolecular free length exhibits same trend with respect to each other but follows opposite trend as compared to acoustic impedance. That is, the adiabatic compressibilities and intermolecular free lengths are surging with surge in mole fraction of EGs as well as with surge in temperature. The opposite behavior among Z and (β , L_f) and same behavior among (β and L_f) is also confirmed from their mathematical expressions. Such surge in β and L_f values and decrement in Z values supports the existence of certain type of interactions in the present systems.

ULTRASONIC ATTENUATION COEFFICIENT (α), RELAXATION TIME (τ)

The ultrasonic attenuation coefficient and relaxation time deals with loss in intensity of ultrasonic wave while propagating through a medium. It is analyzed from the computed values that α values lessen with rise in mole fraction of EGs as well as with rise in temperature. It suggests that the absorption of ultrasonic wave goes on diminishing with surge in EGs' mole fraction and temperature. The described data demonstrate that the values of relaxation time fall with rise in temperature and EGs' mole fraction. More the relaxation time, more is the time taken by the particles to come back to their mean position, hence more is the absorption of ultrasonic waves. Therefore, decrease in τ values indicate that there is less absorption of ultrasonic wave and hence less loss of energy.

FREE VOLUME (V_f), MOLAR VOLUME (V_m), AVAILABLE VOLUME (V_a)

All the values of free volume, molar volume and available volume are found to be inclining with respect to rise in mole fraction of EGs and temperature. In liquids, molecules are free to move within the liquids by following various laws. The free and available volume gives the idea of space available for movement of the molecules of liquid mixtures and the molar volume gives ratio of effective molecular weight and density. It is observed that V_f , V_m and V_a values are surging with surge in temperature but with surge in mole fraction of EGs, V_f and V_a tend to rise whereas V_m tend to fall.

WADA'S CONSTANT (W), RAO'S CONSTANT (R), VANDER WAAL'S CONSTANT (b)

The Wada's constant, Rao's constant and Vander Waal's constant gives the relation between ultrasonic speed, density and viscosity. These constants are independent of temperature. As seen from calculated data the values of W , R and b found to be decreasing with increasing mole fractions of EGs and very slight change is observed in context to temperature. This diminution in constants can be attributed to the diminution in density

and ultrasonic speed. All the constants are linearly varying which shows the presence of specific interactions in the studied systems.

GIBB'S FREE ENERGY (ΔG), INTERNAL PRESSURE (π_i), ENTHALPY (H)

The Gibb's free energy, internal pressure and enthalpy can be related to the transport properties of liquid mixtures. The values for all these three properties as perceived from given plots are decreasing with surge in mole fraction of EGs. The π_i values and H values are decreasing with rise in temperature as well but no particular trend is perceived for Gibb's free energy in context to temperature. This decrease in values of internal pressure is because of reducing viscosities. If the internal pressure increases then, it would be difficult for the molecules of liquid mixtures to move within the liquid and hence more difficult for them to flow. Therefore, lesser the viscosity lesser is pressure and higher the viscosity higher is pressure.

EXCESS MOLAR VOLUME (V^E) AND DEVIATIONS IN ISENTROPIC COMPRESSIBILITY ($\Delta\beta$)

The computed values of excess molar volume and deviations in isentropic compressibility are attributed in Table 4.44 and plotted in **Figures 4.45 to 4.47**. The sign and magnitude of excess functions depends upon the change in properties of liquid mixtures when two or more components mixed together. These contributions can be divided into three types-physical, chemical and structural. The physical contribution comprising of dispersion forces and weak (non-specific) interactions, lead to positive values of V^E . The chemical contribution involves breaking up of the associates present in the pure liquids, lead to increase in volume thus positive V^E values. But some specific interactions such as formation of H-bonding, charge transfer (donor-acceptor) complexes and strong dipole-dipole interactions among the molecules of the mixture, resulting in negative values. Figure 4.45 indicates that the V^E values are negative for all three binary systems over entire mole fraction range and at each investigated temperature. The V^E values are becoming less

negative as the temperature increases, which means at higher temperature the structure of mixtures is less packed. The deep minimum values suggest the formation of strong interactions among the molecules of the mixture components.

Further, the deviations in isentropic compressibility have also been calculated. The values obtained are negative which suggest that there are significant interactions among EGs and glycerol molecules. The glycerol molecules interact strongly with molecules of EGs leading to decrease in compressibility of the binary liquid mixtures which is further reflected by negative $\Delta\beta$ values. For all the studied systems, the values of $\Delta\beta$ become less negative with increase in temperature for entire mole fraction range and at each investigated temperature. The results obtained are following the same trend as of excess molar volumes.

VISCOSITY DEVIATIONS ($\Delta\eta$) AND EXCESS GIBB'S FREE ENERGY OF ACTIVATION (ΔG^{*E})

The values for viscosity deviations and excess Gibb's free energy of activation are given in Table 4.45. The magnitude and sign of $\Delta\eta$ and ΔG^{*E} plays a significant role in describing the molecular rearrangements because of interactions in the liquid mixtures. This rearrangement of molecules can be attributed to specific interactions namely H-bonding, dipole-dipole interactions, and charge transfer among molecules resulting in positive/negative values. For all three binary systems $\Delta\eta$ are negative whereas ΔG^{*E} values are found to be positive over entire mole fraction and at whole temperature range. These negative $\Delta\eta$ values and positive ΔG^{*E} values can be attributed to the presence of significant interactions due to hydrogen bonding among the molecules of EGs and glycerol. Further, the magnitude of ΔG^{*E} follows the order EG>DEG>TEG which suggests that the order of interactions among EG and glycerol molecules will be: EG<DEG<TEG.

THEORETICAL STUDY OF ULTRASONIC SPEEDS

The ultrasonic speeds for the binary liquid mixtures have been computed by some theoretical models given by Nomoto (U_{NOM}), Junjie (U_{JUN}), Van Dael and Vangeel (U_{VDV}) and impedance relation (U_{IMP}). Values obtained from these theoretical models have been compared with the experimental obtained results and percentage deviations have been calculated. The average percentage error (APE) for each set of computed speeds for an entire range of mole fractions has been evaluated. Further, the chi-square test has also been applied to check the goodness of fit of a particular theoretical model. It has been observed that values for APE and chi-square test come out to be least for the theoretical model based on impedance for all three binary systems and at all temperatures. Since the effect of molecular interactions are not considered in theoretical models therefore, the deviations in experimental ultrasonic speeds are observed.

TABLE 4.37: Acoustic impedance (Z) and adiabatic compressibility (β) for binary liquid mixtures of EGs (1) + Glycerol (2) at different temperatures.

Mole fraction of EGs	$Z \times 10^3$ (Kg·m ² ·s ⁻¹)					$\beta \times 10^{-7}$ (Pa ⁻¹)				
	T= 298.15 K	T= 303.15 K	T= 308.15 K	T= 313.15 K	T= 313.15 K	T= 298.15 K	T= 303.15 K	T= 308.15 K	T= 313.15 K	T= 313.15 K
<i>EG + Glycerol</i>										
0.0000	2.415	2.366	2.317	2.293	2.293	2.156	2.242	2.332	2.375	2.375
0.0958	2.387	2.336	2.286	2.259	2.259	2.192	2.282	2.376	2.428	2.428
0.1858	2.357	2.307	2.256	2.227	2.227	2.230	2.323	2.421	2.478	2.478
0.2706	2.328	2.278	2.226	2.195	2.195	2.269	2.364	2.467	2.528	2.528
0.3505	2.297	2.248	2.197	2.165	2.165	2.312	2.407	2.511	2.579	2.579
0.4259	2.265	2.217	2.167	2.134	2.134	2.357	2.455	2.561	2.632	2.632
0.4973	2.228	2.183	2.135	2.101	2.101	2.418	2.513	2.615	2.694	2.694
0.5649	2.185	2.140	2.096	2.062	2.062	2.493	2.591	2.692	2.772	2.772
0.6290	2.138	2.095	2.054	2.022	2.022	2.581	2.680	2.777	2.859	2.859
0.6900	2.090	2.051	2.013	1.983	1.983	2.677	2.773	2.866	2.945	2.945
0.7479	2.044	2.008	1.974	1.946	1.946	2.775	2.869	2.955	3.032	3.032
0.8032	1.999	1.966	1.936	1.910	1.910	2.876	2.966	3.045	3.122	3.122
0.8558	1.956	1.926	1.899	1.875	1.875	2.976	3.063	3.136	3.211	3.211
0.9061	1.915	1.889	1.865	1.842	1.842	3.080	3.157	3.225	3.299	3.299
0.9541	1.875	1.854	1.832	1.809	1.809	3.182	3.249	3.314	3.389	3.389

1.0000	1.837	1.820	1.800	1.778	3.286	3.343	3.403	3.478
<i>DEG + Glycerol</i>								
0.0000	2.415	2.366	2.317	2.293	2.156	2.242	2.332	2.375
0.0584	2.385	2.333	2.285	2.258	2.200	2.291	2.380	2.430
0.1178	2.355	2.301	2.253	2.224	2.244	2.340	2.432	2.487
0.1783	2.323	2.268	2.221	2.190	2.293	2.391	2.486	2.545
0.2399	2.291	2.236	2.189	2.156	2.343	2.445	2.542	2.607
0.3026	2.256	2.204	2.155	2.122	2.399	2.500	2.603	2.672
0.3665	2.222	2.170	2.121	2.088	2.457	2.559	2.667	2.740
0.4316	2.187	2.135	2.087	2.053	2.518	2.624	2.735	2.814
0.4979	2.147	2.096	2.049	2.015	2.592	2.701	2.815	2.897
0.5655	2.096	2.049	2.005	1.972	2.694	2.802	2.914	2.997
0.6345	2.042	1.998	1.959	1.927	2.813	2.918	3.027	3.112
0.7047	1.986	1.947	1.911	1.881	2.945	3.046	3.149	3.234
0.7764	1.929	1.893	1.864	1.835	3.090	3.188	3.280	3.366
0.8494	1.873	1.841	1.815	1.790	3.245	3.337	3.423	3.506
0.9240	1.817	1.789	1.767	1.744	3.413	3.500	3.576	3.657
1.0000	1.759	1.737	1.720	1.700	3.598	3.674	3.738	3.815
<i>TEG + Glycerol</i>								
0.0000	2.415	2.366	2.317	2.293	2.156	2.242	2.332	2.375

0.0584	2.389	2.339	2.289	2.264	2.193	2.281	2.373	2.419
0.1178	2.362	2.310	2.261	2.234	2.232	2.324	2.417	2.466
0.1783	2.332	2.281	2.232	2.204	2.275	2.369	2.464	2.517
0.2399	2.302	2.250	2.202	2.173	2.321	2.418	2.515	2.570
0.3026	2.271	2.218	2.171	2.141	2.370	2.470	2.569	2.628
0.3665	2.237	2.185	2.139	2.108	2.424	2.527	2.627	2.691
0.4316	2.204	2.151	2.105	2.074	2.482	2.589	2.691	2.759
0.4979	2.168	2.116	2.071	2.039	2.545	2.655	2.759	2.834
0.5655	2.128	2.078	2.035	2.002	2.622	2.732	2.836	2.917
0.6345	2.081	2.036	1.995	1.962	2.717	2.823	2.926	3.010
0.7047	2.031	1.990	1.952	1.920	2.828	2.930	3.030	3.115
0.7764	1.977	1.941	1.908	1.877	2.955	3.051	3.145	3.233
0.8494	1.921	1.890	1.860	1.831	3.096	3.186	3.277	3.365
0.9240	1.863	1.836	1.811	1.784	3.258	3.342	3.426	3.514
1.0000	1.803	1.781	1.759	1.734	3.441	3.517	3.595	3.682

TABLE 4.38: Intermolecular free length (L_f) and attenuation (α) for binary liquid mixtures of EGs (1) + Glycerol (2) at different temperatures.

Mole fraction of EGs	$L_f \times 10^9$ (m)					$\alpha \times 10^{-6}$ ($s^2 \cdot m^{-1}$)						
	$T=298.15$ K	$T=303.15$ K	$T=308.15$ K	$T=313.15$ K	$T=298.15$ K	$T=303.15$ K	$T=308.15$ K	$T=313.15$ K	$T=298.15$ K	$T=303.15$ K	$T=308.15$ K	$T=313.15$ K
<i>EG + Glycerol</i>												
0.0000	0.934	0.953	0.971	0.980	2.674	1.870	1.344	0.960	2.674	1.870	1.344	0.960
0.0958	0.942	0.961	0.981	0.991	2.437	1.700	1.220	0.874	2.437	1.700	1.220	0.874
0.1858	0.950	0.970	0.990	1.001	2.217	1.538	1.099	0.788	2.217	1.538	1.099	0.788
0.2706	0.958	0.978	0.999	1.012	2.005	1.380	0.986	0.706	2.005	1.380	0.986	0.706
0.3505	0.967	0.987	1.008	1.022	1.805	1.235	0.880	0.631	1.805	1.235	0.880	0.631
0.4259	0.977	0.997	1.018	1.032	1.615	1.103	0.782	0.561	1.615	1.103	0.782	0.561
0.4973	0.989	1.008	1.029	1.044	1.448	0.983	0.691	0.498	1.448	0.983	0.691	0.498
0.5649	1.004	1.024	1.044	1.059	1.298	0.881	0.615	0.443	1.298	0.881	0.615	0.443
0.6290	1.022	1.041	1.060	1.076	1.159	0.784	0.543	0.392	1.159	0.784	0.543	0.392
0.6900	1.041	1.059	1.077	1.092	1.022	0.690	0.472	0.342	1.022	0.690	0.472	0.342
0.7479	1.060	1.077	1.093	1.108	0.879	0.592	0.405	0.293	0.879	0.592	0.405	0.293
0.8032	1.079	1.096	1.110	1.124	0.731	0.495	0.339	0.248	0.731	0.495	0.339	0.248
0.8558	1.098	1.113	1.127	1.140	0.581	0.395	0.272	0.200	0.581	0.395	0.272	0.200
0.9061	1.116	1.130	1.143	1.155	0.426	0.293	0.204	0.154	0.426	0.293	0.204	0.154
0.9541	1.135	1.147	1.158	1.171	0.261	0.186	0.134	0.104	0.261	0.186	0.134	0.104
1.0000	1.153	1.163	1.174	1.186	0.092	0.073	0.061	0.053	0.092	0.073	0.061	0.053

DEG + Glycerol

0.0000	0.918	0.944	0.971	0.989	2.674	1.870	1.344	0.960
0.0584	0.927	0.954	0.981	1.001	2.458	1.718	1.224	0.876
0.1178	0.936	0.965	0.992	1.012	2.249	1.564	1.108	0.798
0.1783	0.946	0.975	1.003	1.024	2.049	1.415	1.001	0.720
0.2399	0.956	0.986	1.014	1.036	1.852	1.277	0.902	0.648
0.3026	0.968	0.997	1.026	1.049	1.672	1.145	0.809	0.584
0.3665	0.980	1.009	1.039	1.062	1.502	1.020	0.719	0.521
0.4316	0.992	1.021	1.052	1.077	1.336	0.907	0.637	0.463
0.4979	1.006	1.036	1.067	1.092	1.182	0.806	0.563	0.409
0.5655	1.026	1.055	1.086	1.111	1.042	0.711	0.496	0.363
0.6345	1.048	1.077	1.107	1.132	0.919	0.622	0.438	0.320
0.7047	1.072	1.100	1.129	1.154	0.791	0.537	0.382	0.280
0.7764	1.098	1.126	1.152	1.177	0.660	0.448	0.324	0.240
0.8494	1.126	1.152	1.177	1.202	0.500	0.353	0.256	0.196
0.9240	1.154	1.180	1.203	1.227	0.328	0.249	0.180	0.143
1.0000	1.185	1.209	1.230	1.254	0.170	0.142	0.114	0.097

TEG + Glycerol

0.0000	0.918	0.944	0.971	0.989	2.674	1.870	1.344	0.960
0.0584	0.925	0.952	0.980	0.998	2.454	1.709	1.225	0.878

0.1178	0.934	0.961	0.989	1.008	2.238	1.552	1.112	0.798
0.1783	0.942	0.970	0.999	1.018	2.030	1.404	1.005	0.724
0.2399	0.952	0.980	1.009	1.029	1.832	1.265	0.904	0.654
0.3026	0.962	0.991	1.020	1.040	1.651	1.135	0.809	0.588
0.3665	0.973	1.002	1.031	1.053	1.475	1.013	0.721	0.526
0.4316	0.984	1.015	1.044	1.066	1.310	0.898	0.638	0.468
0.4979	0.997	1.027	1.057	1.080	1.154	0.792	0.562	0.414
0.5655	1.012	1.042	1.071	1.096	1.010	0.693	0.492	0.366
0.6345	1.030	1.059	1.088	1.113	0.876	0.602	0.429	0.321
0.7047	1.051	1.079	1.107	1.133	0.746	0.518	0.371	0.279
0.7764	1.074	1.101	1.128	1.154	0.612	0.435	0.313	0.237
0.8494	1.100	1.125	1.152	1.177	0.473	0.345	0.252	0.195
0.9240	1.128	1.153	1.177	1.203	0.334	0.251	0.192	0.155
1.0000	1.159	1.182	1.206	1.232	0.209	0.172	0.142	0.121

TABLE 4.39: Relaxation time (τ) and free volume (V_f) for binary liquid mixtures of EGs (1) + Glycerol (2) at different temperatures.

Mole fraction of EGs	$\tau \times 10^{-4}$ (s)					$V_f \times 10^{-10}$ ($\text{m}^3 \cdot \text{mol}^{-1}$)						
	$T=298.15$ K	$T=303.15$ K	$T=308.15$ K	$T=313.15$ K	$T=298.15$ K	$T=303.15$ K	$T=308.15$ K	$T=313.15$ K	$T=298.15$ K	$T=303.15$ K	$T=308.15$ K	$T=313.15$ K
<i>EG + Glycerol</i>												
0.0000	2.604	1.787	1.262	0.894	0.974	1.767	3.075	5.233				
0.0958	2.363	1.617	1.139	0.808	0.109	0.200	0.349	0.594				
0.1858	2.139	1.455	1.021	0.725	0.124	0.228	0.400	0.683				
0.2706	1.925	1.300	0.911	0.645	0.141	0.263	0.464	0.794				
0.3505	1.723	1.158	0.809	0.573	0.163	0.305	0.541	0.927				
0.4259	1.534	1.027	0.714	0.506	0.190	0.357	0.638	1.094				
0.4973	1.363	0.909	0.627	0.446	0.223	0.422	0.760	1.300				
0.5649	1.209	0.806	0.552	0.393	0.264	0.500	0.909	1.554				
0.6290	1.065	0.708	0.482	0.344	0.317	0.602	1.104	1.881				
0.6900	0.926	0.615	0.415	0.297	0.389	0.741	1.372	2.320				
0.7479	0.786	0.522	0.352	0.252	0.497	0.943	1.747	2.946				
0.8032	0.645	0.431	0.292	0.211	0.666	1.251	2.297	3.816				
0.8558	0.506	0.339	0.232	0.168	0.955	1.780	3.226	5.314				
0.9061	0.367	0.249	0.172	0.128	1.546	2.819	5.010	7.923				
0.9541	0.222	0.156	0.112	0.086	3.279	5.634	9.464	14.261				
1.0000	0.077	0.061	0.051	0.044	15.844	23.098	30.753	39.195				

DEG + Glycerol

0.0000	2.604	1.787	1.262	0.894	0.974	1.767	3.075	5.233
0.0584	2.376	1.630	1.141	0.809	0.115	0.210	0.370	0.630
0.1178	2.158	1.474	1.026	0.732	0.138	0.253	0.449	0.760
0.1783	1.951	1.323	0.919	0.655	0.166	0.308	0.548	0.932
0.2399	1.750	1.184	0.823	0.585	0.202	0.376	0.671	1.145
0.3026	1.567	1.054	0.732	0.522	0.247	0.465	0.830	1.410
0.3665	1.395	0.931	0.644	0.462	0.305	0.580	1.044	1.761
0.4316	1.231	0.821	0.566	0.406	0.383	0.728	1.316	2.219
0.4979	1.077	0.722	0.495	0.355	0.488	0.921	1.677	2.832
0.5655	0.936	0.628	0.430	0.311	0.633	1.191	2.170	3.621
0.6345	0.811	0.541	0.375	0.271	0.827	1.569	2.806	4.681
0.7047	0.686	0.459	0.322	0.233	1.126	2.120	3.716	6.169
0.7764	0.561	0.377	0.269	0.197	1.613	3.017	5.125	8.335
0.8494	0.418	0.291	0.209	0.158	2.667	4.694	7.887	12.239
0.9240	0.268	0.202	0.144	0.114	5.499	8.629	14.519	21.112
1.0000	0.136	0.112	0.090	0.076	16.155	22.016	31.391	40.848

TEG + Glycerol

0.0000	2.604	1.787	1.262	0.894	0.974	1.767	3.075	5.233
0.0584	2.376	1.624	1.144	0.812	0.118	0.216	0.377	0.641

0.1178	2.153	1.467	1.032	0.735	0.145	0.267	0.467	0.791
0.1783	1.940	1.318	0.926	0.662	0.180	0.333	0.583	0.984
0.2399	1.739	1.179	0.828	0.594	0.226	0.419	0.735	1.234
0.3026	1.556	1.050	0.736	0.530	0.285	0.532	0.937	1.563
0.3665	1.379	0.930	0.650	0.470	0.365	0.683	1.205	2.006
0.4316	1.215	0.818	0.571	0.414	0.473	0.888	1.572	2.599
0.4979	1.061	0.714	0.498	0.364	0.623	1.169	2.072	3.403
0.5655	0.918	0.619	0.432	0.318	0.836	1.565	2.768	4.501
0.6345	0.785	0.531	0.373	0.276	1.150	2.136	3.743	6.037
0.7047	0.658	0.451	0.318	0.237	1.640	2.981	5.178	8.270
0.7764	0.532	0.373	0.265	0.198	2.485	4.351	7.453	11.785
0.8494	0.403	0.290	0.210	0.160	4.165	6.978	11.648	17.839
0.9240	0.279	0.207	0.157	0.125	8.039	12.790	19.884	28.524
1.0000	0.170	0.139	0.114	0.096	18.790	25.922	35.869	46.871

TABLE 4.40: Molar volume (V_m) and available volume (V_a) for binary liquid mixtures of EGs (1) + Glycerol (2) at different temperatures.

Mole fraction of EGs	V_m ($\text{m}^3 \cdot \text{mol}^{-1}$)					V_a ($\text{m}^3 \cdot \text{mol}^{-1}$)						
	$T=298.15$ K	$T=303.15$ K	$T=308.15$ K	$T=313.15$ K	$T=298.15$ K	$T=303.15$ K	$T=308.15$ K	$T=313.15$ K	$T=298.15$ K	$T=303.15$ K	$T=308.15$ K	$T=313.15$ K
<i>EG + Glycerol</i>												
0.0000	73.21	73.38	73.57	73.76	-14.64	-13.08	-11.54	-10.90	-11.54	-13.08	-11.54	-10.90
0.0958	71.45	71.63	71.83	72.03	-13.92	-12.34	-10.81	-10.07	-13.92	-12.34	-10.81	-10.07
0.1858	69.82	69.99	70.21	70.42	-13.19	-11.64	-10.12	-9.35	-13.19	-11.64	-10.12	-9.35
0.2706	68.29	68.47	68.69	68.91	-12.52	-11.02	-9.49	-8.68	-12.52	-11.02	-9.49	-8.68
0.3505	66.88	67.05	67.28	67.49	-11.84	-10.38	-8.93	-8.07	-11.84	-10.38	-8.93	-8.07
0.4259	65.55	65.72	65.95	66.16	-11.17	-9.75	-8.33	-7.46	-11.17	-9.75	-8.33	-7.46
0.4973	64.31	64.47	64.71	64.92	-10.32	-9.01	-7.71	-6.79	-10.32	-9.01	-7.71	-6.79
0.5649	63.15	63.31	63.55	63.75	-9.32	-8.05	-6.85	-5.96	-9.32	-8.05	-6.85	-5.96
0.6290	62.06	62.22	62.46	62.65	-8.23	-7.03	-5.96	-5.10	-8.23	-7.03	-5.96	-5.10
0.6900	61.04	61.19	61.43	61.62	-7.15	-6.05	-5.10	-4.32	-7.15	-6.05	-5.10	-4.32
0.7479	60.08	60.22	60.47	60.64	-6.12	-5.13	-4.32	-3.59	-6.12	-5.13	-4.32	-3.59
0.8032	59.17	59.30	59.55	59.71	-5.17	-4.26	-3.58	-2.89	-5.17	-4.26	-3.58	-2.89
0.8558	58.30	58.43	58.68	58.83	-4.29	-3.47	-2.88	-2.25	-4.29	-3.47	-2.88	-2.25
0.9061	57.48	57.60	57.85	58.00	-3.45	-2.77	-2.26	-1.67	-3.45	-2.77	-2.26	-1.67
0.9541	56.69	56.82	57.06	57.20	-2.69	-2.13	-1.69	-1.11	-2.69	-2.13	-1.69	-1.11
1.0000	55.95	56.06	56.30	56.44	-1.97	-1.53	-1.15	-0.59	-1.97	-1.53	-1.15	-0.59

<i>DEG + Glycerol</i>										
0.0000	73.21	73.38	73.57	73.76	-14.64	-13.08	-11.54	-10.90		
0.0584	74.26	74.52	74.73	74.97	-14.21	-12.63	-11.13	-10.41		
0.1178	75.33	75.68	75.93	76.20	-13.76	-12.17	-10.67	-9.90		
0.1783	76.46	76.88	77.14	77.46	-13.26	-11.71	-10.18	-9.37		
0.2399	77.63	78.10	78.39	78.74	-12.77	-11.19	-9.67	-8.79		
0.3026	78.87	79.35	79.68	80.04	-12.19	-10.67	-9.09	-8.18		
0.3665	80.17	80.66	81.01	81.38	-11.61	-10.11	-8.48	-7.52		
0.4316	81.51	82.03	82.39	82.77	-11.00	-9.46	-7.82	-6.79		
0.4979	82.93	83.48	83.83	84.23	-10.21	-8.67	-7.01	-5.95		
0.5655	84.49	85.03	85.36	85.79	-9.01	-7.54	-5.94	-4.91		
0.6345	86.09	86.65	86.97	87.42	-7.58	-6.21	-4.71	-3.70		
0.7047	87.78	88.34	88.64	89.11	-6.01	-4.76	-3.41	-2.43		
0.7764	89.53	90.12	90.39	90.85	-4.33	-3.20	-2.02	-1.07		
0.8494	91.37	91.94	92.20	92.62	-2.59	-1.59	-0.53	0.36		
0.9240	93.27	93.83	94.05	94.42	-0.75	0.15	1.04	1.90		
1.0000	95.30	95.76	95.94	96.26	1.20	1.96	2.69	3.50		
<i>TEG + Glycerol</i>										
0.0000	73.21	73.38	73.57	73.76	-14.64	-13.08	-11.54	-10.90		
0.0584	75.54	75.75	76.00	76.23	-14.58	-12.99	-11.43	-10.76		

0.1178	78.01	78.31	78.57	78.86	-14.49	-12.87	-11.28	-10.58
0.1783	80.66	81.01	81.31	81.64	-14.36	-12.70	-11.08	-10.35
0.2399	83.48	83.90	84.23	84.59	-14.18	-12.49	-10.84	-10.06
0.3026	86.53	86.97	87.34	87.73	-13.97	-12.22	-10.54	-9.70
0.3665	89.79	90.27	90.65	91.08	-13.69	-11.89	-10.18	-9.26
0.4316	93.26	93.80	94.22	94.66	-13.32	-11.47	-9.73	-8.71
0.4979	96.99	97.57	98.03	98.50	-12.86	-10.95	-9.18	-8.06
0.5655	101.04	101.63	102.11	102.63	-12.17	-10.25	-8.48	-7.24
0.6345	105.44	106.03	106.51	107.08	-11.10	-9.26	-7.51	-6.24
0.7047	110.24	110.83	111.31	111.90	-9.73	-8.00	-6.30	-5.01
0.7764	115.48	116.04	116.51	117.11	-8.08	-6.45	-4.85	-3.53
0.8494	121.18	121.69	122.17	122.77	-6.12	-4.59	-3.08	-1.75
0.9240	127.40	127.89	128.32	128.90	-3.77	-2.37	-0.97	0.37
1.0000	134.19	134.65	135.02	135.58	-0.95	0.28	1.57	2.90

TABLE 4.41: Wada's Constant (W) and Rao's Constant (R) for binary liquid mixtures of EGs (1) + Glycerol (2) at different temperatures.

Mole fraction of EGs	W ($\text{m}^3 \cdot \text{mol}^{-1} \cdot \text{Pa}^{1/7}$)					R ($\text{m}^3 \cdot \text{mol}^{-1} \cdot \text{m}^{1/3} \cdot \text{s}^{1/3}$)						
	$T=298.15$ K	$T=303.15$ K	$T=308.15$ K	$T=313.15$ K	$T=298.15$ K	$T=303.15$ K	$T=308.15$ K	$T=313.15$ K	$T=298.15$ K	$T=303.15$ K	$T=308.15$ K	$T=313.15$ K
<i>EG + Glycerol</i>												
0.0000	655.95	653.90	651.91	651.86	909.86	906.55	903.33	903.25	909.86	906.55	903.33	903.25
0.0958	638.75	636.63	634.78	634.60	886.76	883.34	880.35	880.06	886.76	883.34	880.35	880.06
0.1858	622.57	620.53	618.75	618.59	865.05	861.74	858.86	858.59	865.05	861.74	858.86	858.59
0.2706	607.50	605.54	603.79	603.58	844.86	841.68	838.84	838.51	844.86	841.68	838.84	838.51
0.3505	593.32	591.43	589.86	589.49	825.88	822.80	820.27	819.66	825.88	822.80	820.27	819.66
0.4259	579.96	578.08	576.61	576.21	808.01	804.95	802.57	801.91	808.01	804.95	802.57	801.91
0.4973	566.94	565.24	564.04	563.48	790.48	787.71	785.77	784.86	790.48	787.71	785.77	784.86
0.5649	554.26	552.60	551.67	551.10	773.33	770.61	769.10	768.19	773.33	770.61	769.10	768.19
0.6290	542.00	540.44	539.79	539.25	756.67	754.13	753.08	752.19	756.67	754.13	753.08	752.19
0.6900	530.31	528.92	528.54	528.10	740.79	738.51	737.90	737.19	740.79	738.51	737.90	737.19
0.7479	519.24	518.01	517.96	517.55	725.75	723.74	723.66	723.00	725.75	723.74	723.66	723.00
0.8032	508.80	507.69	507.94	507.52	711.61	709.81	710.20	709.51	711.61	709.81	710.20	709.51
0.8558	498.91	497.97	498.38	498.04	698.23	696.70	697.36	696.80	698.23	696.70	697.36	696.80
0.9061	489.47	488.81	489.38	489.07	685.46	684.38	685.31	684.82	685.46	684.38	685.31	684.82
0.9541	480.54	480.13	480.83	480.47	673.41	672.74	673.88	673.30	673.41	672.74	673.88	673.30
1.0000	472.04	471.85	472.64	472.30	661.95	661.65	662.94	662.38	661.95	661.65	662.94	662.38

DEG + Glycerol

0.0000	655.95	653.90	651.91	651.86	909.86	906.55	903.33	903.25
0.0584	663.53	661.98	660.22	660.38	920.79	918.28	915.43	915.69
0.1178	671.16	670.27	668.79	669.02	931.77	930.32	927.92	928.30
0.1783	679.10	678.79	677.30	677.82	943.22	942.71	940.30	941.15
0.2399	687.39	687.33	686.04	686.65	955.22	955.12	953.03	954.01
0.3026	696.05	696.16	694.99	695.60	967.79	967.97	966.07	967.06
0.3665	705.03	705.30	704.20	704.67	980.86	981.30	979.51	980.27
0.4316	714.33	714.66	713.59	713.99	994.42	994.95	993.21	993.87
0.4979	723.83	724.29	723.11	723.57	1008.27	1009.03	1007.10	1007.85
0.5655	733.34	733.89	732.69	733.39	1022.13	1023.01	1021.06	1022.21
0.6345	742.66	743.55	742.44	743.33	1035.64	1037.07	1035.28	1036.73
0.7047	752.28	753.44	752.46	753.54	1049.59	1051.49	1049.90	1051.66
0.7764	762.07	763.62	762.84	763.84	1063.82	1066.34	1065.06	1066.70
0.8494	772.26	774.04	773.37	774.22	1078.65	1081.54	1080.46	1081.85
0.9240	782.67	784.55	784.00	784.57	1093.80	1096.87	1095.98	1096.91
1.0000	793.71	795.14	794.68	795.02	1109.96	1112.30	1111.53	1112.10

TEG + Glycerol

0.0000	655.95	653.90	651.91	651.86	909.86	906.55	903.33	903.25
0.0584	675.22	673.32	671.77	671.95	937.04	933.97	931.46	931.74

0.1178	695.53	694.20	692.65	693.19	965.68	963.52	961.01	961.89
0.1783	717.25	716.17	714.80	715.56	996.36	994.61	992.40	993.63
0.2399	740.26	739.59	738.29	739.17	1028.87	1027.79	1025.69	1027.11
0.3026	764.94	764.30	763.21	764.17	1063.82	1062.79	1061.02	1062.57
0.3665	791.20	790.74	789.69	790.71	1101.02	1100.27	1098.57	1100.22
0.4316	819.01	818.84	817.96	818.86	1140.39	1140.12	1138.70	1140.15
0.4979	848.70	848.68	848.00	848.85	1182.47	1182.42	1181.32	1182.70
0.5655	880.42	880.40	879.87	880.76	1227.40	1227.37	1226.51	1227.95
0.6345	914.12	914.22	913.70	914.84	1275.12	1275.27	1274.42	1276.29
0.7047	950.22	950.58	950.07	951.36	1326.20	1326.79	1325.96	1328.06
0.7764	989.19	989.49	989.15	990.39	1381.41	1381.91	1381.35	1383.37
0.8494	1031.14	1031.25	1031.16	1032.30	1440.83	1441.02	1440.86	1442.73
0.9240	1076.22	1076.45	1076.20	1077.16	1504.63	1505.01	1504.60	1506.16
1.0000	1124.68	1125.12	1124.62	1125.43	1573.12	1573.84	1573.03	1574.35

TABLE 4.42: Vander Waal's constant (b) and Gibb's Free Energy (ΔG) for binary liquid mixtures of EGs (1) + Glycerol (2) at different temperatures.

Mole fraction of EGs	b ($\text{m}^3 \cdot \text{mol}^{-1}$)					$\Delta G \times 10^{20}$ ($\text{kJ} \cdot \text{mol}^{-1}$)				
	$T=298.15$ K	$T=303.15$ K	$T=308.15$ K	$T=313.15$ K	$T=298.15$ K	$T=303.15$ K	$T=308.15$ K	$T=313.15$ K	$T=308.15$ K	$T=313.15$ K
<i>EG + Glycerol</i>										
0.0000	61.00	61.15	61.31	61.47	8.719	8.715	8.718	8.718	8.718	8.718
0.0958	59.54	59.69	59.86	60.03	8.679	8.673	8.674	8.674	8.674	8.674
0.1858	58.18	58.33	58.51	58.68	8.638	8.629	8.628	8.628	8.628	8.627
0.2706	56.91	57.06	57.24	57.43	8.595	8.582	8.579	8.579	8.579	8.577
0.3505	55.73	55.88	56.06	56.24	8.549	8.533	8.529	8.529	8.529	8.525
0.4259	54.63	54.77	54.96	55.14	8.501	8.484	8.476	8.476	8.476	8.472
0.4973	53.60	53.73	53.92	54.10	8.453	8.432	8.421	8.421	8.421	8.417
0.5649	52.63	52.76	52.96	53.13	8.404	8.382	8.367	8.367	8.367	8.362
0.6290	51.72	51.85	52.05	52.21	8.352	8.328	8.309	8.309	8.309	8.304
0.6900	50.87	50.99	51.20	51.35	8.294	8.269	8.245	8.245	8.245	8.241
0.7479	50.06	50.18	50.39	50.53	8.226	8.200	8.175	8.175	8.175	8.170
0.8032	49.31	49.42	49.63	49.76	8.145	8.120	8.095	8.095	8.095	8.093
0.8558	48.59	48.69	48.90	49.03	8.045	8.020	7.997	7.997	7.997	7.996
0.9061	47.90	48.00	48.21	48.33	7.913	7.891	7.870	7.870	7.870	7.879
0.9541	47.25	47.35	47.55	47.67	7.706	7.696	7.688	7.688	7.688	7.707

1.0000	46.62	46.72	46.92	47.03	7.273	7.301	7.352	7.414
<i>DEG + Glycerol</i>								
0.0000	61.00	61.15	61.31	61.47	8.719	8.715	8.718	8.718
0.0584	61.89	62.10	62.28	62.48	8.682	8.677	8.675	8.675
0.1178	62.78	63.07	63.28	63.50	8.642	8.634	8.630	8.631
0.1783	63.72	64.07	64.28	64.55	8.600	8.589	8.583	8.583
0.2399	64.69	65.08	65.32	65.62	8.556	8.543	8.536	8.534
0.3026	65.73	66.13	66.40	66.70	8.510	8.494	8.486	8.485
0.3665	66.81	67.22	67.51	67.82	8.463	8.442	8.432	8.432
0.4316	67.92	68.36	68.66	68.98	8.411	8.390	8.377	8.377
0.4979	69.11	69.56	69.86	70.19	8.356	8.336	8.320	8.319
0.5655	70.41	70.85	71.14	71.49	8.298	8.278	8.261	8.261
0.6345	71.74	72.21	72.48	72.85	8.240	8.215	8.202	8.202
0.7047	73.15	73.62	73.87	74.26	8.171	8.147	8.137	8.137
0.7764	74.61	75.10	75.33	75.70	8.088	8.064	8.061	8.065
0.8494	76.14	76.62	76.84	77.18	7.966	7.957	7.954	7.969
0.9240	77.73	78.19	78.38	78.69	7.785	7.803	7.797	7.828
1.0000	79.42	79.80	79.95	80.22	7.507	7.559	7.594	7.653
<i>TEG + Glycerol</i>								
0.0000	61.00	61.15	61.31	61.47	8.719	8.715	8.718	8.718

0.0584	62.95	63.13	63.34	63.53	8.681	8.675	8.676	8.676
0.1178	65.01	65.26	65.48	65.72	8.641	8.632	8.632	8.633
0.1783	67.22	67.51	67.76	68.03	8.598	8.588	8.586	8.588
0.2399	69.57	69.92	70.19	70.49	8.553	8.541	8.539	8.541
0.3026	72.11	72.48	72.78	73.11	8.507	8.493	8.489	8.492
0.3665	74.82	75.23	75.55	75.90	8.458	8.442	8.436	8.440
0.4316	77.71	78.17	78.52	78.89	8.406	8.388	8.381	8.385
0.4979	80.82	81.31	81.69	82.09	8.350	8.332	8.323	8.329
0.5655	84.20	84.69	85.10	85.52	8.290	8.272	8.262	8.271
0.6345	87.87	88.36	88.76	89.23	8.226	8.208	8.200	8.210
0.7047	91.86	92.36	92.76	93.25	8.154	8.139	8.132	8.143
0.7764	96.23	96.70	97.09	97.59	8.066	8.060	8.054	8.067
0.8494	100.99	101.41	101.81	102.31	7.952	7.955	7.955	7.975
0.9240	106.17	106.58	106.93	107.42	7.800	7.815	7.832	7.868
1.0000	111.82	112.21	112.52	112.98	7.598	7.648	7.694	7.755

TABLE 4.43: Internal pressure (π_i) and Enthalpy (H) for binary liquid mixtures of EGs (1) + Glycerol (2) at different temperatures.

Mole fraction of EGs	$\pi_i \times 10^6$ (Pa)					$H \times 10^7$ (J·mol ⁻¹)					
	T=298.15 K	T=303.15 K	T=308.15 K	T=313.15 K	T=298.15 K	T=303.15 K	T=308.15 K	T=313.15 K	T=298.15 K	T=308.15 K	T=313.15 K
<i>EG + Glycerol</i>											
0.0000	1.326	1.104	0.931	0.791	9.707	8.100	6.851	5.837	6.851	5.837	5.837
0.0958	1.297	1.077	0.907	0.771	9.264	7.714	6.517	5.552	6.517	5.552	5.552
0.1858	1.264	1.047	0.880	0.747	8.827	7.329	6.177	5.260	6.177	5.260	5.260
0.2706	1.228	1.013	0.850	0.721	8.385	6.937	5.840	4.966	5.840	4.966	4.966
0.3505	1.187	0.977	0.819	0.694	7.940	6.551	5.509	4.682	5.509	4.682	4.682
0.4259	1.143	0.940	0.785	0.665	7.494	6.175	5.180	4.402	5.180	4.402	4.402
0.4973	1.097	0.900	0.750	0.636	7.057	5.806	4.854	4.130	4.854	4.130	4.130
0.5649	1.050	0.861	0.715	0.607	6.630	5.451	4.546	3.868	4.546	3.868	3.868
0.6290	0.999	0.819	0.678	0.576	6.201	5.094	4.236	3.608	4.236	3.608	3.608
0.6900	0.943	0.773	0.638	0.543	5.757	4.728	3.919	3.346	3.919	3.346	3.346
0.7479	0.879	0.721	0.595	0.507	5.280	4.340	3.597	3.073	3.597	3.073	3.073
0.8032	0.805	0.663	0.548	0.470	4.764	3.929	3.266	2.805	3.266	2.805	2.805
0.8558	0.721	0.595	0.495	0.425	4.204	3.476	2.902	2.499	2.902	2.499	2.499
0.9061	0.620	0.515	0.431	0.375	3.564	2.968	2.494	2.178	2.494	2.178	2.178
0.9541	0.487	0.413	0.352	0.312	2.761	2.346	2.009	1.782	2.009	1.782	1.782
1.0000	0.291	0.260	0.240	0.224	1.626	1.459	1.350	1.266	1.350	1.266	1.266

DEG + Glycerol

0.0000	1.326	1.104	0.931	0.791	9.707	8.100	6.851	5.837
0.0584	1.241	1.032	0.867	0.736	9.218	7.687	6.476	5.516
0.1178	1.159	0.960	0.804	0.684	8.732	7.262	6.101	5.210
0.1783	1.079	0.889	0.744	0.632	8.249	6.839	5.739	4.895
0.2399	1.000	0.823	0.688	0.583	7.763	6.427	5.394	4.594
0.3026	0.925	0.759	0.634	0.539	7.294	6.023	5.052	4.310
0.3665	0.853	0.697	0.581	0.495	6.836	5.624	4.707	4.025
0.4316	0.782	0.639	0.532	0.453	6.375	5.243	4.381	3.747
0.4979	0.713	0.584	0.485	0.413	5.915	4.877	4.065	3.475
0.5655	0.646	0.530	0.440	0.375	5.457	4.504	3.753	3.221
0.6345	0.583	0.477	0.399	0.340	5.022	4.134	3.466	2.976
0.7047	0.520	0.426	0.358	0.306	4.561	3.764	3.177	2.731
0.7764	0.455	0.374	0.318	0.274	4.073	3.369	2.873	2.487
0.8494	0.380	0.318	0.272	0.238	3.468	2.927	2.505	2.202
0.9240	0.294	0.256	0.219	0.196	2.743	2.405	2.057	1.848
1.0000	0.202	0.185	0.167	0.155	1.929	1.772	1.602	1.492

TEG + Glycerol

0.0000	1.326	1.104	0.931	0.791	9.707	8.100	6.851	5.837
0.0584	1.218	1.011	0.851	0.724	9.197	7.658	6.469	5.516

0.1178	1.113	0.921	0.775	0.659	8.681	7.215	6.093	5.200
0.1783	1.013	0.837	0.704	0.599	8.169	6.779	5.722	4.892
0.2399	0.918	0.757	0.636	0.543	7.664	6.353	5.359	4.590
0.3026	0.830	0.683	0.573	0.489	7.179	5.937	5.004	4.294
0.3665	0.745	0.613	0.514	0.439	6.691	5.531	4.658	4.001
0.4316	0.666	0.547	0.458	0.393	6.215	5.132	4.319	3.717
0.4979	0.592	0.486	0.407	0.350	5.744	4.744	3.991	3.443
0.5655	0.522	0.429	0.360	0.310	5.278	4.364	3.674	3.180
0.6345	0.457	0.376	0.316	0.273	4.815	3.990	3.369	2.925
0.7047	0.394	0.327	0.276	0.239	4.342	3.623	3.069	2.672
0.7764	0.332	0.280	0.237	0.206	3.839	3.244	2.759	2.411
0.8494	0.271	0.231	0.198	0.174	3.284	2.815	2.416	2.133
0.9240	0.211	0.183	0.160	0.144	2.682	2.339	2.055	1.854
1.0000	0.153	0.140	0.127	0.118	2.056	1.880	1.717	1.598

TABLE 4.44: The calculated values of excess molar volume (V^E) and deviations in isentropic compressibility ($\Delta\beta$) of activation for binary liquid mixtures of EGs (1) + Glycerol (2) at different temperatures.

Mole fraction of EGs	V^E ($\text{m}^3 \cdot \text{mol}^{-1}$)										$\Delta\beta$ (Pa^{-1})									
	$T=298.15$ K	$T=303.15$ K	$T=308.15$ K	$T=313.15$ K	$T=298.15$ K	$T=303.15$ K	$T=308.15$ K	$T=313.15$ K	$T=298.15$ K	$T=303.15$ K	$T=308.15$ K	$T=313.15$ K	$T=298.15$ K	$T=303.15$ K	$T=308.15$ K	$T=313.15$ K				
<i>EG + Glycerol</i>																				
0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000				
0.0958	-0.1006	-0.0968	-0.0850	-0.0678	-7.2929	-6.5376	-5.8282	-5.3103	-10.9408	-10.1965	-14.5080	-18.2753	-21.2921	-23.0073	-22.6299	-21.0369				
0.1858	-0.1833	-0.1708	-0.1546	-0.1195	-13.6274	-12.3341	-10.9408	-10.1965	-19.2818	-17.6300	-15.4907	-14.5080	-19.6298	-18.2753	-22.8627	-21.0369				
0.2706	-0.2416	-0.2262	-0.2075	-0.1619	-24.0445	-22.0359	-19.6298	-18.2753	-28.0269	-25.5945	-22.7313	-21.2921	-30.0374	-27.6858	-24.8965	-23.0073				
0.3505	-0.2796	-0.2624	-0.2417	-0.1963	-30.0374	-27.6858	-24.8965	-23.0073	-30.0374	-27.6858	-24.8965	-23.0073	-30.0374	-27.6858	-24.8965	-23.0073				
0.4259	-0.3016	-0.2860	-0.2651	-0.2182	-29.1752	-27.2917	-24.4644	-22.6299	-29.1752	-27.2917	-24.4644	-22.6299	-29.1752	-27.2917	-24.4644	-22.6299				
0.4973	-0.3096	-0.2966	-0.2746	-0.2289	-27.0109	-25.4532	-22.8627	-21.0369	-27.0109	-25.4532	-22.8627	-21.0369	-27.0109	-25.4532	-22.8627	-21.0369				
0.5649	-0.3048	-0.2900	-0.2645	-0.2226	-24.3426	-22.8030	-20.4782	-19.1419	-24.3426	-22.8030	-20.4782	-19.1419	-24.3426	-22.8030	-20.4782	-19.1419				
0.6290	-0.2877	-0.2723	-0.2484	-0.2080	-21.1255	-19.6683	-17.8471	-16.8453	-21.1255	-19.6683	-17.8471	-16.8453	-21.1255	-19.6683	-17.8471	-16.8453				
0.6900	-0.2578	-0.2439	-0.2212	-0.1860	-17.3680	-15.9865	-14.6984	-13.9092	-17.3680	-15.9865	-14.6984	-13.9092	-17.3680	-15.9865	-14.6984	-13.9092				
0.7479	-0.2229	-0.2125	-0.1882	-0.1613	-13.1525	-12.1389	-11.2277	-10.8451	-13.1525	-12.1389	-11.2277	-10.8451	-13.1525	-12.1389	-11.2277	-10.8451				
0.8032	-0.1780	-0.1722	-0.1480	-0.1309	-8.7345	-8.2407	-7.6942	-7.5994	-8.7345	-8.2407	-7.6942	-7.5994	-8.7345	-8.2407	-7.6942	-7.5994				
0.8558	-0.1337	-0.1294	-0.1129	-0.0992	-4.4089	-4.2972	-3.9812	-3.8415	-4.4089	-4.2972	-3.9812	-3.8415	-4.4089	-4.2972	-3.9812	-3.8415				
0.9061	-0.0901	-0.0858	-0.0737	-0.0639																
0.9541	-0.0473	-0.0432	-0.0341	-0.0313																

1.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
<i>DEG + Glycerol</i>										
0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
0.0584	-0.2323	-0.1702	-0.1477	-0.1029	-4.0791	-3.4797	-3.3476	-2.8672	-2.8672	-2.8672
0.1178	-0.4764	-0.3353	-0.2739	-0.2074	-8.2039	-7.0365	-6.5179	-5.7378	-5.7378	-5.7378
0.1783	-0.6871	-0.4917	-0.4200	-0.3109	-12.0431	-10.6140	-9.6590	-8.6315	-8.6315	-8.6315
0.2399	-0.8781	-0.6555	-0.5525	-0.4196	-15.9688	-14.0769	-12.7104	-11.3349	-11.3349	-11.3349
0.3026	-1.0183	-0.8023	-0.6653	-0.5258	-19.3519	-17.5274	-15.4705	-13.9231	-13.9231	-13.9231
0.3665	-1.1387	-0.9224	-0.7575	-0.6281	-22.7526	-20.7930	-18.0318	-16.3172	-16.3172	-16.3172
0.4316	-1.2351	-1.0145	-0.8354	-0.7011	-26.0525	-23.5922	-20.3377	-18.2819	-18.2819	-18.2819
0.4979	-1.2754	-1.0504	-0.8773	-0.7351	-28.2244	-25.4239	-21.7087	-19.5416	-19.5416	-19.5416
0.5655	-1.2153	-1.0130	-0.8599	-0.6954	-27.7919	-25.0083	-21.3522	-19.2322	-19.2322	-19.2322
0.6345	-1.1341	-0.9326	-0.7919	-0.6155	-25.8224	-23.2187	-19.7194	-17.6901	-17.6901	-17.6901
0.7047	-0.9973	-0.8117	-0.6919	-0.5065	-22.7086	-20.4784	-17.4276	-15.5802	-15.5802	-15.5802
0.7764	-0.8268	-0.6378	-0.5457	-0.3848	-18.5916	-16.5849	-14.3574	-12.7443	-12.7443	-12.7443
0.8494	-0.6067	-0.4466	-0.3709	-0.2556	-13.6017	-12.1739	-10.3244	-9.2502	-9.2502	-9.2502
0.9240	-0.3521	-0.2271	-0.1867	-0.1291	-7.5411	-6.5194	-5.5553	-4.9273	-4.9273	-4.9273
1.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
<i>TEG + Glycerol</i>										
0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000

0.0584	-0.2269	-0.2051	-0.1467	-0.1210	-1.8065	-1.4581	-1.1716	-1.0672
0.1178	-0.4561	-0.3602	-0.2974	-0.2278	-3.6697	-2.8253	-2.3562	-2.1171
0.1783	-0.6507	-0.5214	-0.4294	-0.3364	-5.4719	-4.2583	-3.5188	-3.2108
0.2399	-0.8390	-0.6535	-0.5483	-0.4420	-7.3328	-5.6408	-4.6898	-4.2871
0.3026	-0.9861	-0.7913	-0.6558	-0.5385	-9.1978	-7.0860	-5.8887	-5.3646
0.3665	-1.1128	-0.8926	-0.7488	-0.6175	-11.0423	-8.4887	-7.0930	-6.3404
0.4316	-1.2425	-0.9772	-0.8085	-0.6853	-12.9435	-9.8368	-8.2046	-7.2392
0.4979	-1.3437	-1.0575	-0.8599	-0.7287	-14.7772	-11.2046	-9.3088	-7.9965
0.5655	-1.3840	-1.1078	-0.8975	-0.7494	-15.8897	-12.1039	-10.1098	-8.4524
0.6345	-1.3540	-1.1037	-0.9047	-0.7318	-15.7081	-12.1436	-10.1683	-8.5118
0.7047	-1.2483	-1.0127	-0.8364	-0.6635	-14.5751	-11.2865	-9.5012	-8.0414
0.7764	-1.0476	-0.8691	-0.7130	-0.5631	-12.7005	-9.7118	-8.3675	-7.0910
0.8494	-0.7721	-0.6732	-0.5214	-0.4086	-10.1313	-7.4875	-6.4195	-5.4712
0.9240	-0.4221	-0.3693	-0.2882	-0.2305	-6.5493	-4.2271	-3.7209	-3.1945
1.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000

TABLE 4.45: The calculated values of viscosity deviations ($\Delta \eta$) and excess Gibb's free energy (ΔG^{*E}) of activation for binary liquid mixtures of EGs (1) + Glycerol (2) at different temperatures.

Mole fraction of EGs	$\Delta \eta$ (mPa·s)					ΔG^{*E} (kJ·mol ⁻¹)					
	T=298.15 K	T=303.15 K	T=308.15 K	T=313.15 K	T=298.15 K	T=303.15 K	T=308.15 K	T=313.15 K	T=298.15 K	T=303.15 K	T=313.15 K
<i>EG + Glycerol</i>											
0.0000	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
0.0958	-12.04	-10.70	-8.50	-6.53	657.3	618.6	575.1	532.7	575.1	532.7	532.7
0.1858	-21.25	-19.56	-16.30	-12.36	1248.4	1169.1	1076.9	995.0	1076.9	995.0	995.0
0.2706	-29.14	-27.27	-22.17	-17.17	1772.5	1650.9	1518.1	1392.6	1518.1	1392.6	1392.6
0.3505	-35.36	-32.55	-25.98	-20.14	2232.7	2073.9	1904.5	1739.9	1904.5	1739.9	1739.9
0.4259	-39.49	-35.19	-28.51	-21.93	2632.2	2443.6	2231.1	2032.8	2231.1	2032.8	2032.8
0.4973	-41.26	-35.95	-29.68	-22.49	2973.5	2757.3	2500.8	2274.9	2500.8	2274.9	2274.9
0.5649	-40.35	-34.66	-29.00	-21.96	3259.6	3018.9	2722.7	2467.3	2722.7	2467.3	2467.3
0.6290	-37.53	-32.13	-27.32	-20.56	3485.5	3220.3	2885.2	2606.4	2885.2	2606.4	2606.4
0.6900	-33.55	-28.54	-24.87	-18.45	3641.7	3356.4	2980.4	2687.4	2980.4	2687.4	2687.4
0.7479	-29.22	-24.53	-21.38	-15.96	3709.2	3408.7	3009.3	2693.8	3009.3	2693.8	2693.8
0.8032	-24.32	-19.78	-17.05	-12.53	3669.4	3365.9	2958.8	2642.3	2958.8	2642.3	2642.3
0.8558	-18.22	-14.78	-12.73	-9.52	3495.8	3185.7	2774.5	2444.9	2774.5	2444.9	2444.9
0.9061	-11.83	-9.40	-8.31	-5.93	3100.9	2804.7	2399.5	2110.7	2399.5	2110.7	2110.7
0.9541	-6.22	-4.40	-3.99	-2.89	2239.6	2014.8	1671.7	1430.6	2014.8	1671.7	1430.6

1.0000	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
<i>DEG + Glycerol</i>													
0.0000	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
0.0584	-44.23	-30.60	-22.63	-16.02	657.3	618.6	575.1	532.7					
0.1178	-81.01	-57.99	-41.84	-30.29	1248.4	1169.1	1076.9	995.0					
0.1783	-111.13	-80.39	-57.33	-40.85	1772.5	1650.9	1518.1	1392.6					
0.2399	-134.94	-96.72	-68.08	-49.06	2232.7	2073.9	1904.5	1739.9					
0.3026	-150.49	-107.82	-75.62	-53.96	2632.2	2443.6	2231.1	2032.8					
0.3665	-158.35	-114.28	-80.52	-57.52	2973.5	2757.3	2500.8	2274.9					
0.4316	-160.50	-115.08	-82.17	-58.68	3259.6	3018.9	2722.7	2467.3					
0.4979	-157.26	-111.08	-80.73	-57.60	3485.5	3220.3	2885.2	2606.4					
0.5655	-148.98	-104.57	-76.19	-53.95	3641.7	3356.4	2980.4	2687.4					
0.6345	-133.79	-94.07	-68.69	-47.76	3709.2	3408.7	3009.3	2693.8					
0.7047	-115.30	-81.35	-59.21	-39.90	3669.4	3365.9	2958.8	2642.3					
0.7764	-92.43	-64.92	-45.95	-30.80	3495.8	3185.7	2774.5	2444.9					
0.8494	-64.04	-44.05	-31.57	-21.39	3100.9	2804.7	2399.5	2110.7					
0.9240	-36.18	-23.43	-15.99	-10.92	2239.6	2014.8	1671.7	1430.6					
1.0000					0.0	0.0	0.0	0.0					
<i>TEG + Glycerol</i>													
0.0000	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00

0.0584	-56.72	-39.29	-27.93	-19.52	77.8	48.8	26.9	12.7
0.1178	-107.37	-75.81	-53.27	-38.05	153.6	95.1	54.7	25.9
0.1783	-150.56	-105.54	-73.90	-52.08	231.2	144.9	83.7	42.9
0.2399	-185.13	-129.04	-89.98	-62.94	313.4	199.8	116.4	61.8
0.3026	-209.48	-146.19	-101.66	-70.96	409.2	259.7	152.2	83.0
0.3665	-226.92	-157.77	-110.65	-76.82	502.3	325.2	192.3	103.0
0.4316	-234.09	-162.74	-114.21	-80.71	602.4	393.0	234.2	127.7
0.4979	-235.72	-161.61	-113.96	-80.86	703.6	467.8	283.1	158.8
0.5655	-228.20	-156.14	-109.10	-76.86	803.9	542.6	336.2	198.6
0.6345	-210.41	-144.63	-100.38	-70.23	894.7	615.3	397.4	242.9
0.7047	-186.55	-125.75	-88.67	-60.66	961.2	684.4	453.0	282.0
0.7764	-155.11	-102.61	-71.17	-49.70	968.3	717.0	478.2	287.2
0.8494	-112.88	-75.35	-50.36	-35.92	854.6	633.7	403.8	226.4
0.9240	-62.48	-40.70	-27.71	-20.43	557.6	374.6	223.8	112.9
1.0000	0.00	0.00	0.00	0.00	0.0	0.0	0.0	0.0

Table 4.46: Ultrasonic speeds computed from theoretical models: Nomoto's relation (U_{NOM}) and impedance relation (U_{IMP}) for binary liquid mixtures of EGs (1) + Glycerol (2) at different temperatures.

Mole fraction	U_{NOM} ($\text{m}\cdot\text{s}^{-1}$)					U_{IMP} ($\text{m}\cdot\text{s}^{-1}$)					
	$T=298.15$ K	$T=303.15$ K	$T=308.15$ K	$T=313.15$ K	$T=298.15$ K	$T=303.15$ K	$T=308.15$ K	$T=313.15$ K	$T=298.15$ K	$T=303.15$ K	$T=313.15$ K
<i>EG + Glycerol</i>											
0.0000	1780.2	1748.3	1716.9	1703.4	1920.0	1885.2	1851.0	1836.4	1851.0	1816.0	1799.6
0.0958	1761.2	1730.9	1701.2	1687.7	1897.5	1864.6	1832.4	1817.6	1832.4	1799.6	1799.6
0.1858	1742.7	1714.0	1686.0	1672.4	1875.8	1844.7	1814.4	1799.6	1814.4	1799.6	1799.6
0.2706	1724.6	1697.5	1671.0	1657.4	1855.0	1825.7	1797.2	1782.3	1797.2	1782.3	1782.3
0.3505	1707.0	1681.4	1656.5	1642.7	1835.0	1807.4	1780.6	1765.7	1780.6	1765.7	1765.7
0.4259	1689.8	1665.7	1642.3	1628.4	1815.7	1789.7	1764.7	1749.6	1764.7	1749.6	1749.6
0.4973	1673.0	1650.3	1628.4	1614.4	1797.1	1772.7	1749.3	1734.2	1749.3	1734.2	1734.2
0.5649	1656.6	1635.3	1614.8	1600.8	1779.2	1756.3	1734.5	1719.2	1734.5	1719.2	1719.2
0.6290	1640.5	1620.6	1601.5	1587.4	1761.9	1740.5	1720.2	1704.9	1720.2	1704.9	1704.9
0.6900	1624.8	1606.3	1588.5	1574.3	1745.2	1725.3	1706.4	1691.0	1706.4	1691.0	1691.0
0.7479	1609.5	1592.2	1575.8	1561.6	1729.1	1710.5	1693.0	1677.6	1693.0	1677.6	1677.6
0.8032	1594.6	1578.5	1563.3	1549.1	1713.6	1696.3	1680.1	1664.6	1680.1	1664.6	1664.6
0.8558	1579.9	1565.1	1551.2	1536.8	1698.5	1682.5	1667.7	1652.1	1667.7	1652.1	1652.1
0.9061	1565.6	1551.9	1539.3	1524.8	1684.0	1669.2	1655.6	1639.9	1655.6	1639.9	1639.9
0.9541	1551.6	1539.1	1527.6	1513.1	1669.9	1656.3	1643.9	1628.2	1643.9	1628.2	1628.2

1.0000	1537.9	1526.5	1516.2	1501.7	1656.2	1643.8	1632.6	1616.8
<i>DEG + Glycerol</i>								
0.0000	1780.2	1748.3	1716.9	1703.4	1920.0	1885.2	1851.0	1836.4
0.0584	1755.5	1725.1	1695.4	1682.1	1902.3	1868.7	1835.6	1821.1
0.1178	1731.4	1702.6	1674.5	1661.3	1884.0	1851.7	1819.8	1805.3
0.1783	1707.9	1680.7	1654.2	1641.0	1865.2	1834.1	1803.4	1789.1
0.2399	1685.0	1659.3	1634.3	1621.2	1845.7	1815.9	1786.5	1772.2
0.3026	1662.7	1638.5	1615.0	1602.0	1825.6	1797.1	1769.0	1754.8
0.3665	1641.0	1618.2	1596.1	1583.2	1804.8	1777.7	1750.9	1736.8
0.4316	1619.8	1598.4	1577.6	1564.8	1783.3	1757.6	1732.2	1718.2
0.4979	1599.1	1579.0	1559.6	1546.9	1761.0	1736.7	1712.8	1698.9
0.5655	1578.9	1560.2	1542.1	1529.4	1737.9	1715.1	1692.7	1678.9
0.6345	1559.3	1541.8	1524.9	1512.4	1713.9	1692.8	1671.9	1658.2
0.7047	1540.1	1523.8	1508.2	1495.7	1689.1	1669.5	1650.3	1636.7
0.7764	1521.3	1506.3	1491.8	1479.4	1663.3	1645.4	1627.8	1614.3
0.8494	1503.0	1489.1	1475.8	1463.5	1636.6	1620.4	1604.5	1591.1
0.9240	1485.1	1472.4	1460.2	1448.0	1608.7	1594.3	1580.3	1567.0
1.0000	1467.6	1456.0	1444.9	1432.8	1579.8	1567.2	1555.1	1541.9
<i>TEG + Glycerol</i>								
0.0000	1780.2	1748.3	1716.9	1703.4	1920.0	1885.2	1851.0	1836.4

0.0584	1758.0	1727.5	1697.5	1684.0	1908.4	1874.4	1840.9	1826.3
0.1178	1736.3	1707.3	1678.7	1665.0	1896.1	1862.9	1830.1	1815.5
0.1783	1715.2	1687.6	1660.2	1646.5	1882.9	1850.6	1818.7	1804.0
0.2399	1694.5	1668.3	1642.2	1628.4	1868.9	1837.5	1806.4	1791.7
0.3026	1674.4	1649.5	1624.7	1610.8	1853.8	1823.4	1793.3	1778.5
0.3665	1654.7	1631.1	1607.5	1593.5	1837.7	1808.3	1779.2	1764.4
0.4316	1635.5	1613.1	1590.7	1576.7	1820.3	1792.0	1764.0	1749.1
0.4979	1616.7	1595.6	1574.3	1560.2	1801.4	1774.5	1747.5	1732.7
0.5655	1598.4	1578.4	1558.3	1544.1	1781.1	1755.4	1729.7	1714.8
0.6345	1580.4	1561.6	1542.6	1528.4	1758.9	1734.7	1710.4	1695.4
0.7047	1562.9	1545.2	1527.2	1513.0	1734.8	1712.2	1689.3	1674.2
0.7764	1545.8	1529.2	1512.2	1498.0	1708.3	1687.4	1666.2	1651.0
0.8494	1529.0	1513.5	1497.5	1483.2	1679.2	1660.2	1640.8	1625.5
0.9240	1512.6	1498.2	1483.2	1468.8	1647.0	1630.1	1612.6	1597.2
1.0000	1496.6	1483.2	1469.1	1454.8	1611.3	1596.7	1581.4	1565.8

Table 4.47: Ultrasonic speeds computed from theoretical models: Van Dael and Vangeel (U_{VDV}) and Junjie's equation (U_{JUN}) for binary liquid mixtures of EGs (1) + Glycerol (2) at different temperatures.

Mole fraction	U_{VDV} ($m \cdot s^{-1}$)					U_{JUN} ($m \cdot s^{-1}$)						
	$T=298.15$ K	$T=303.15$ K	$T=308.15$ K	$T=313.15$ K	$T=298.15$ K	$T=303.15$ K	$T=308.15$ K	$T=313.15$ K	$T=298.15$ K	$T=303.15$ K	$T=308.15$ K	$T=313.15$ K
<i>EG + Glycerol</i>												
0.0000	1920.0	1885.2	1851.0	1836.4	1920.0	1885.2	1851.0	1836.4	1920.0	1885.2	1851.0	1836.4
0.0958	1864.0	1833.6	1803.8	1789.1	1891.8	1859.7	1828.1	1813.3	1891.8	1859.7	1828.1	1813.3
0.1858	1820.0	1793.0	1766.6	1751.7	1865.8	1836.2	1806.9	1792.0	1865.8	1836.2	1806.9	1792.0
0.2706	1785.0	1760.6	1737.0	1722.0	1841.9	1814.4	1787.3	1772.3	1841.9	1814.4	1787.3	1772.3
0.3505	1756.9	1734.7	1713.2	1698.1	1819.8	1794.2	1769.1	1754.0	1819.8	1794.2	1769.1	1754.0
0.4259	1734.2	1713.7	1694.1	1678.9	1799.2	1775.5	1752.1	1736.9	1799.2	1775.5	1752.1	1736.9
0.4973	1715.9	1696.9	1678.7	1663.5	1780.2	1758.1	1736.4	1721.0	1780.2	1758.1	1736.4	1721.0
0.5649	1701.1	1683.3	1666.3	1651.1	1762.5	1741.8	1721.6	1706.2	1762.5	1741.8	1721.6	1706.2
0.6290	1689.2	1672.4	1656.5	1641.2	1745.9	1726.6	1707.8	1692.4	1745.9	1726.6	1707.8	1692.4
0.6900	1679.7	1663.8	1648.9	1633.5	1730.5	1712.4	1694.9	1679.4	1730.5	1712.4	1694.9	1679.4
0.7479	1672.2	1657.1	1643.0	1627.5	1716.0	1699.1	1682.9	1667.3	1716.0	1699.1	1682.9	1667.3
0.8032	1666.4	1652.0	1638.6	1623.1	1702.5	1686.6	1671.5	1655.9	1702.5	1686.6	1671.5	1655.9
0.8558	1662.2	1648.3	1635.6	1620.0	1689.8	1674.9	1660.9	1645.2	1689.8	1674.9	1660.9	1645.2
0.9061	1659.1	1645.8	1633.6	1618.0	1677.9	1663.9	1650.9	1635.2	1677.9	1663.9	1650.9	1635.2
0.9541	1657.2	1644.4	1632.7	1617.0	1666.7	1653.5	1641.5	1625.7	1666.7	1653.5	1641.5	1625.7

1.0000	1656.2	1643.8	1632.6	1616.8	1656.2	1643.8	1632.6	1616.8
<i>DEG + Glycerol</i>								
0.0000	1920.0	1885.2	1851.0	1836.4	1920.0	1885.2	1851.0	1836.4
0.0584	1896.0	1863.0	1830.6	1816.1	1881.9	1849.8	1818.5	1804.0
0.1178	1872.2	1841.0	1810.3	1795.9	1847.2	1817.6	1788.9	1774.4
0.1783	1848.6	1819.1	1790.1	1775.8	1815.6	1788.2	1761.7	1747.3
0.2399	1825.2	1797.4	1770.0	1755.8	1786.7	1761.2	1736.7	1722.4
0.3026	1802.0	1775.8	1750.0	1735.8	1760.1	1736.3	1713.6	1699.4
0.3665	1778.9	1754.3	1730.1	1716.0	1735.6	1713.4	1692.2	1678.2
0.4316	1756.1	1733.0	1710.3	1696.3	1712.9	1692.2	1672.5	1658.5
0.4979	1733.5	1711.8	1690.6	1676.7	1691.9	1672.5	1654.1	1640.2
0.5655	1711.0	1690.8	1671.0	1657.2	1672.4	1654.2	1636.9	1623.2
0.6345	1688.7	1669.8	1651.4	1637.7	1654.3	1637.2	1621.0	1607.3
0.7047	1666.6	1649.1	1632.0	1618.4	1637.3	1621.3	1606.0	1592.5
0.7764	1644.6	1628.4	1612.6	1599.1	1621.5	1606.4	1592.1	1578.6
0.8494	1622.9	1607.9	1593.4	1580.0	1606.7	1592.5	1579.0	1565.6
0.9240	1601.2	1587.5	1574.2	1560.9	1592.8	1579.4	1566.7	1553.4
1.0000	1579.8	1567.2	1555.1	1541.9	1579.8	1567.2	1555.1	1541.9
<i>TEG + Glycerol</i>								
0.0000	1920.0	1885.2	1851.0	1836.4	1920.0	1885.2	1851.0	1836.4

0.0584	1900.2	1866.4	1833.1	1818.5	1886.6	1854.2	1822.4	1807.5
0.1178	1880.3	1847.5	1815.2	1800.6	1856.0	1825.8	1796.0	1780.9
0.1783	1860.3	1828.5	1797.2	1782.6	1827.8	1799.6	1771.6	1756.4
0.2399	1840.1	1809.4	1779.1	1764.5	1801.9	1775.5	1749.1	1733.7
0.3026	1819.8	1790.2	1760.9	1746.3	1777.9	1753.1	1728.2	1712.7
0.3665	1799.3	1770.9	1742.7	1728.1	1755.7	1732.3	1708.8	1693.2
0.4316	1778.7	1751.6	1724.5	1709.8	1735.0	1712.9	1690.7	1675.0
0.4979	1758.0	1732.1	1706.2	1691.5	1715.7	1694.9	1673.7	1658.1
0.5655	1737.2	1712.7	1688.0	1673.2	1697.8	1678.0	1657.9	1642.2
0.6345	1716.3	1693.2	1669.8	1655.0	1681.0	1662.2	1643.1	1627.4
0.7047	1695.3	1673.7	1651.7	1636.8	1665.2	1647.4	1629.2	1613.5
0.7764	1674.3	1654.2	1633.8	1618.7	1650.5	1633.6	1616.1	1600.5
0.8494	1653.2	1634.9	1616.0	1600.8	1636.6	1620.5	1603.9	1588.2
0.9240	1632.2	1615.7	1598.5	1583.1	1623.6	1608.3	1592.3	1576.7
1.0000	1611.3	1596.7	1581.4	1565.8	1611.3	1596.7	1581.4	1565.8

Table 4.48: Percentage deviations of experimental ultrasonic speeds from computed values using theoretical models: Nomoto's relation (U_{NOM}) and impedance relation (U_{IMP}) for binary liquid mixtures of EGs (1) + Glycerol (2) at different temperatures.

Mole fraction of EGs	% U_{NOM}										% U_{IMP}		
	$T=298.15$ K	$T=303.15$ K	$T=308.15$ K	$T=313.15$ K	$T=298.15$ K	$T=303.15$ K	$T=308.15$ K	$T=313.15$ K	$T=308.15$ K	$T=313.15$ K	$T=313.15$ K		
<i>EG + Glycerol</i>													
0.0000	7.2814	7.2644	7.2474	7.2401	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	
0.0958	7.8669	7.7127	7.5828	7.4565	0.7401	0.5886	0.4588	0.3318	0.4588	0.3318	0.4588	0.3318	
0.1858	8.3899	8.1483	7.9067	7.7267	1.3933	1.1448	0.8881	0.7042	0.8881	0.7042	0.8881	0.7042	
0.2706	8.9039	8.6062	8.2398	8.0058	2.0189	1.7077	1.3113	1.0703	1.3113	1.0703	1.3113	1.0703	
0.3505	9.3565	9.0031	8.6027	8.2893	2.5621	2.1890	1.7519	1.4262	1.7519	1.4262	1.7519	1.4262	
0.4259	9.7628	9.3395	8.8698	8.5366	3.0401	2.5904	2.0758	1.7294	2.0758	1.7294	2.0758	1.7294	
0.4973	9.8954	9.5013	9.0610	8.6498	3.2102	2.7907	2.3055	1.8757	2.3055	1.8757	2.3055	1.8757	
0.5649	9.7835	9.3206	8.8991	8.5068	3.1048	2.6104	2.1443	1.7350	2.1443	1.7350	2.1443	1.7350	
0.6290	9.4788	8.9944	8.6333	8.2585	2.7801	2.2621	1.8605	1.4701	1.8605	1.4701	1.8605	1.4701	
0.6900	9.0946	8.6359	8.3339	8.0518	2.3586	1.8679	1.5304	1.2395	1.5304	1.2395	1.5304	1.2395	
0.7479	8.7105	8.2919	8.0808	7.8618	1.9264	1.4789	1.2402	1.0170	1.2402	1.0170	1.2402	1.0170	
0.8032	8.3433	7.9535	7.8276	7.6514	1.5020	1.0856	0.9407	0.7631	1.0856	0.9407	1.0856	0.7631	
0.8558	8.0165	7.6707	7.5916	7.4900	1.1110	0.7426	0.6510	0.5532	0.6510	0.5532	0.6510	0.5532	
0.9061	7.6838	7.4524	7.4131	7.3659	0.7044	0.4599	0.4148	0.3750	0.4148	0.3750	0.4148	0.3750	
0.9541	7.4124	7.2906	7.2666	7.2241	0.3547	0.2294	0.2052	0.1699	0.2052	0.1699	0.2052	0.1699	
1.0000	7.1442	7.1373	7.1309	7.1219	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	
APE	8.5703	8.2702	8.0429	7.8398	1.6754	1.3593	1.1112	0.9038	1.1112	0.9038	1.1112	0.9038	

Chi Square	236.5500	215.3475	199.1810	186.1895	11.9698	8.0433	5.2243	3.4009
<i>DEG + Glycerol</i>								
0.0000	7.2814	7.2644	7.2474	7.2401	0.0000	0.0000	0.0000	0.0000
0.0584	7.9082	7.8008	7.7673	7.6837	0.2043	0.1285	0.1396	0.0539
0.1178	8.5052	8.3278	8.2395	8.1043	0.4362	0.3036	0.2809	0.1358
0.1783	9.0343	8.8362	8.6695	8.5072	0.6554	0.5169	0.4308	0.2534
0.2399	9.5638	9.2919	9.0677	8.8522	0.9380	0.7328	0.6021	0.3641
0.3026	9.9923	9.7301	9.4041	9.1598	1.1748	0.9913	0.7635	0.4919
0.3665	10.4123	10.1264	9.6989	9.4198	1.4693	1.2679	0.9392	0.6278
0.4316	10.8049	10.4359	9.9418	9.6111	1.8031	1.5154	1.1200	0.7510
0.4979	11.0123	10.5971	10.0393	9.7014	2.0054	1.6688	1.2058	0.8284
0.5655	10.8295	10.4273	9.8935	9.5870	1.8540	1.5306	1.0921	0.7497
0.6345	10.4285	10.0798	9.5909	9.3201	1.5433	1.2739	0.8783	0.5762
0.7047	9.9122	9.6362	9.2279	9.0045	1.1930	0.9942	0.6753	0.4270
0.7764	9.3062	9.0861	8.8023	8.6162	0.8385	0.6868	0.4860	0.2811
0.8494	8.6497	8.5133	8.2886	8.1693	0.5308	0.4506	0.2893	0.1604
0.9240	7.9179	7.8315	7.7173	7.6438	0.2515	0.1995	0.1256	0.0502
1.0000	7.1004	7.0929	7.0857	7.0778	0.0000	0.0000	0.0000	0.0000
APE	9.2912	9.0674	8.7926	8.6061	0.9311	0.7663	0.5643	0.3594
Chi Square	277.6076	258.6970	237.5337	224.1714	3.7522	2.5412	1.3255	0.5672
<i>TEG + Glycerol</i>								
0.0000	7.2814	7.2644	7.2474	7.2401	0.0000	0.0000	0.0000	0.0000

0.0584	7.9060	7.8311	7.7784	7.7663	0.0251	-0.0048	-0.0109	-0.0262
0.1178	8.4804	8.3528	8.2551	8.2425	0.0582	0.0010	-0.0244	-0.0496
0.1783	9.0004	8.8254	8.6830	8.6690	0.0982	0.0159	-0.0317	-0.0667
0.2399	9.4712	9.2440	9.0623	9.0361	0.1551	0.0390	-0.0285	-0.0842
0.3026	9.8979	9.6091	9.3934	9.3489	0.2400	0.0756	-0.0097	-0.0919
0.3665	10.2614	9.9205	9.6710	9.5918	0.3379	0.1317	0.0247	-0.1008
0.4316	10.5615	10.1633	9.8849	9.7645	0.4564	0.1979	0.0704	-0.1047
0.4979	10.7881	10.3417	10.0345	9.8607	0.5934	0.2880	0.1350	-0.1014
0.5655	10.8409	10.3840	10.0724	9.8530	0.6487	0.3329	0.1762	-0.1111
0.6345	10.6346	10.2403	9.9381	9.7334	0.5414	0.2908	0.1397	-0.1295
0.7047	10.2399	9.9246	9.6576	9.4873	0.3695	0.1947	0.0707	-0.1561
0.7764	9.7045	9.4552	9.2626	9.1152	0.2098	0.0873	0.0246	-0.1697
0.8494	9.0305	8.8456	8.7087	8.5996	0.0949	0.0113	-0.0219	-0.1635
0.9240	8.1754	8.0643	7.9977	7.9325	0.0159	-0.0326	-0.0338	-0.1131
1.0000	7.1187	7.1103	7.1013	7.0921	0.0000	0.0000	0.0000	0.0000
APE	9.3370	9.0985	8.9218	8.8333	0.2403	0.1018	0.0300	-0.0918
Chi Square	282.5130	262.2199	247.0456	239.2787	0.3024	0.0687	0.0146	0.0297

Table 4.49: Percentage deviations of experimental ultrasonic speeds from computed values using theoretical models: Van Dael and Vangeel (U_{VDV}) and Junjie's equation (U_{JUN}) for binary liquid mixtures of EGs (1) + Glycerol (2) at different temperatures.

Mole fraction of EGs	% U_{VDV}										% U_{JUN}		
	$T=298.15$ K	$T=303.15$ K	$T=308.15$ K	$T=313.15$ K	$T=298.15$ K	$T=303.15$ K	$T=308.15$ K	$T=313.15$ K	$T=308.15$ K	$T=313.15$ K	$T=313.15$ K	$T=313.15$ K	
<i>EG + Glycerol</i>													
0.0958	2.4919	2.2396	2.0079	1.8991	1.0370	0.8482	0.6902	0.5682					
0.1858	4.3277	3.9185	3.4995	3.3470	1.9176	1.6044	1.2989	1.1242					
0.2706	5.7161	5.2100	4.6192	4.4189	2.7105	2.3150	1.8559	1.6271					
0.3505	6.7066	6.1226	5.4739	5.1965	3.3691	2.8992	2.3898	2.0789					
0.4259	7.3887	6.7250	5.9957	5.7003	3.9176	3.3641	2.7722	2.4420					
0.4973	7.5828	6.9502	6.2515	5.8760	4.1209	3.5944	3.0296	2.6171					
0.5649	7.3575	6.6616	5.9897	5.6320	4.0162	3.4163	2.8709	2.4787					
0.6290	6.7931	6.0878	5.4918	5.1490	3.6626	3.0433	2.5651	2.1910					
0.6900	6.0263	5.3649	4.8493	4.5981	3.1844	2.5993	2.1903	1.9138					
0.7479	5.1553	4.5571	4.1600	3.9695	2.6690	2.1369	1.8339	1.6231					
0.8032	4.2107	3.6678	3.3886	3.2371	2.1373	1.6489	1.4488	1.2815					
0.8558	3.2281	2.7603	2.5633	2.4842	1.6166	1.1910	1.0555	0.9656					
0.9061	2.1686	1.8537	1.7356	1.7079	1.0599	0.7750	0.6992	0.6647					
0.9541	1.1108	0.9484	0.8865	0.8573	0.5412	0.3946	0.3544	0.3218					
1.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000					
APE	4.3915	3.9417	3.5570	3.3796	2.2475	1.8644	1.5659	1.3686					
Chi Square	80.8153	64.2045	50.7797	44.9414	21.1244	14.5932	9.9979	7.4679					

DEG + Glycerol

0.0584	0.5356	0.4317	0.4131	0.3299	1.2763	1.1375	1.0700	0.9931
0.1178	1.0629	0.8780	0.7994	0.6594	2.3816	2.1371	1.9743	1.8461
0.1783	1.5402	1.3284	1.1640	0.9941	3.2950	3.0066	2.7343	2.5801
0.2399	2.0409	1.7455	1.5179	1.2897	4.1059	3.7244	3.3737	3.1650
0.3026	2.4543	2.1667	1.8278	1.5680	4.7199	4.3401	3.8713	3.6332
0.3665	2.8805	2.5651	2.1154	1.8176	5.2466	4.8378	4.2577	3.9831
0.4316	3.2983	2.8917	2.3690	2.0152	5.6750	5.1788	4.5294	4.1998
0.4979	3.5364	3.0794	2.4871	2.1255	5.8462	5.3051	4.5935	4.2554
0.5655	3.3727	2.9301	2.3632	2.0360	5.5492	5.0288	4.3510	4.0451
0.6345	2.9936	2.6101	2.0915	1.8035	4.9699	4.5160	3.8976	3.6279
0.7047	2.5112	2.2082	1.7767	1.5406	4.2206	3.8564	3.3387	3.1175
0.7764	1.9538	1.7137	1.4166	1.2217	3.3311	3.0416	2.6745	2.4907
0.8494	1.3644	1.2177	0.9841	0.8622	2.3452	2.1630	1.8798	1.7650
0.9240	0.7166	0.6274	0.5127	0.4410	1.2381	1.1301	0.9887	0.9207
APE	1.8913	1.6496	1.3649	1.1690	3.3875	3.0877	2.7209	2.5389
Chi Square	14.4396	10.8114	7.1379	5.1738	45.7410	37.2392	28.0796	24.0867

TEG + Glycerol

0.0584	0.4534	0.4200	0.4108	0.3971	1.1687	1.0702	0.9969	1.0037
0.1178	0.8884	0.8245	0.7930	0.7711	2.1724	1.9905	1.8427	1.8579
0.1783	1.3000	1.2080	1.1517	1.1216	3.0216	2.7696	2.5552	2.5753
0.2399	1.6932	1.5648	1.4861	1.4370	3.7341	3.4135	3.1445	3.1556

0.3026	2.0730	1.8943	1.7955	1.7221	4.3259	3.9318	3.6189	3.6130
0.3665	2.4180	2.1959	2.0735	1.9590	4.7852	4.3324	3.9801	3.9383
0.4316	2.7276	2.4522	2.3076	2.1461	5.1191	4.6057	4.2231	4.1370
0.4979	2.9901	2.6671	2.4960	2.2756	5.3230	4.7620	4.3522	4.2079
0.5655	3.0961	2.7617	2.5857	2.3164	5.2956	4.7295	4.3211	4.1259
0.6345	2.9523	2.6807	2.5097	2.2581	4.9496	4.4588	4.0690	3.8859
0.7047	2.6356	2.4383	2.2939	2.0833	4.3630	3.9671	3.6258	3.4753
0.7764	2.1974	2.0530	1.9703	1.7899	3.5881	3.2761	3.0272	2.8963
0.8494	1.6395	1.5373	1.4873	1.3561	2.6289	2.4012	2.2271	2.1319
0.9240	0.9148	0.8546	0.8427	0.7691	1.4401	1.3096	1.2281	1.1741
1.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
APE	1.7487	1.5970	1.5128	1.4001	3.2447	2.9386	2.7007	2.6361
Chi Square	12.0957	9.8161	8.5965	7.2082	41.3658	33.0719	27.3012	25.6567

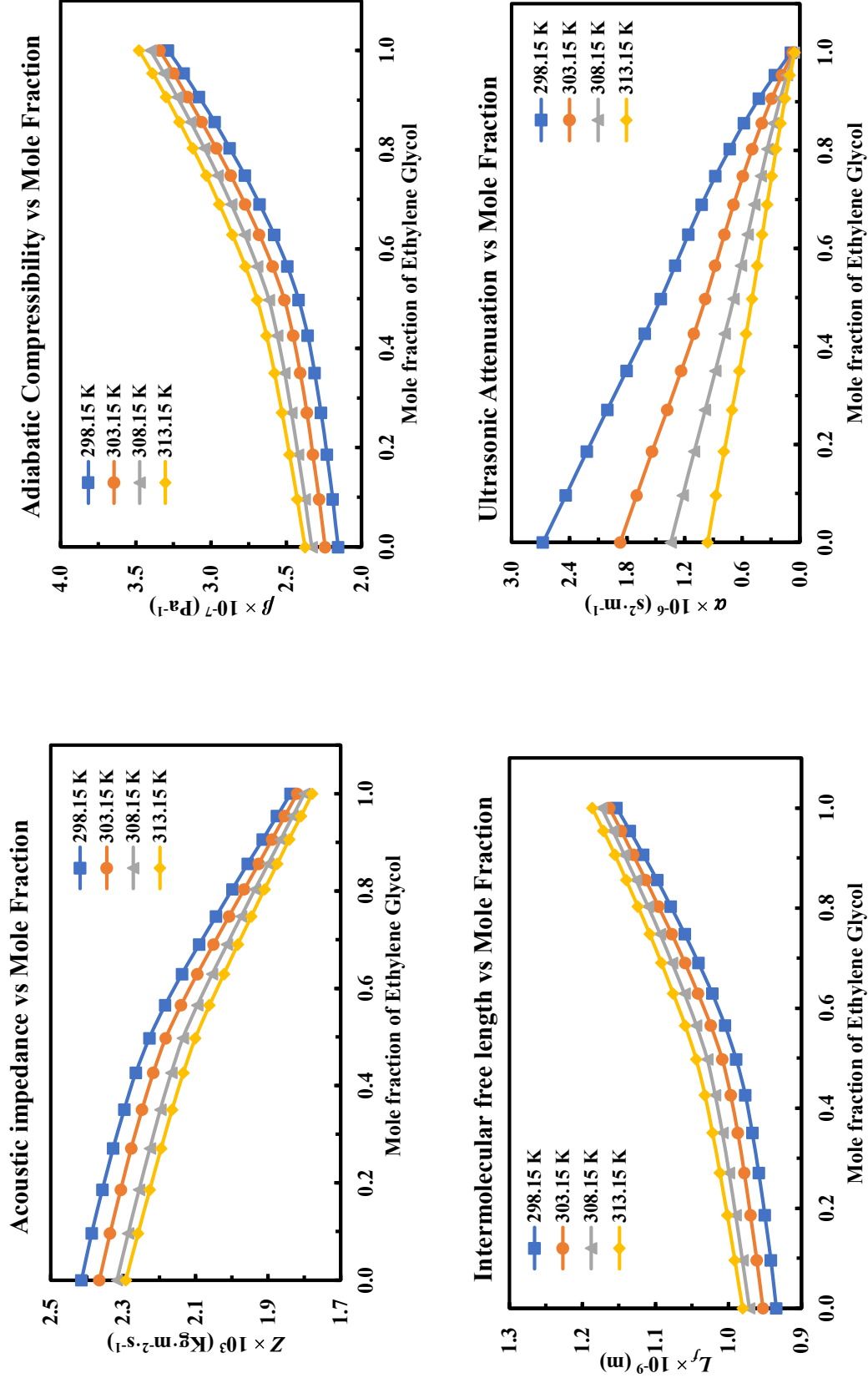


Figure 4.32: Plots of acoustic impedance, intermolecular free length and ultrasonic attenuation in the binary mixtures of Ethylene Glycol (1) + Glycerol (2).

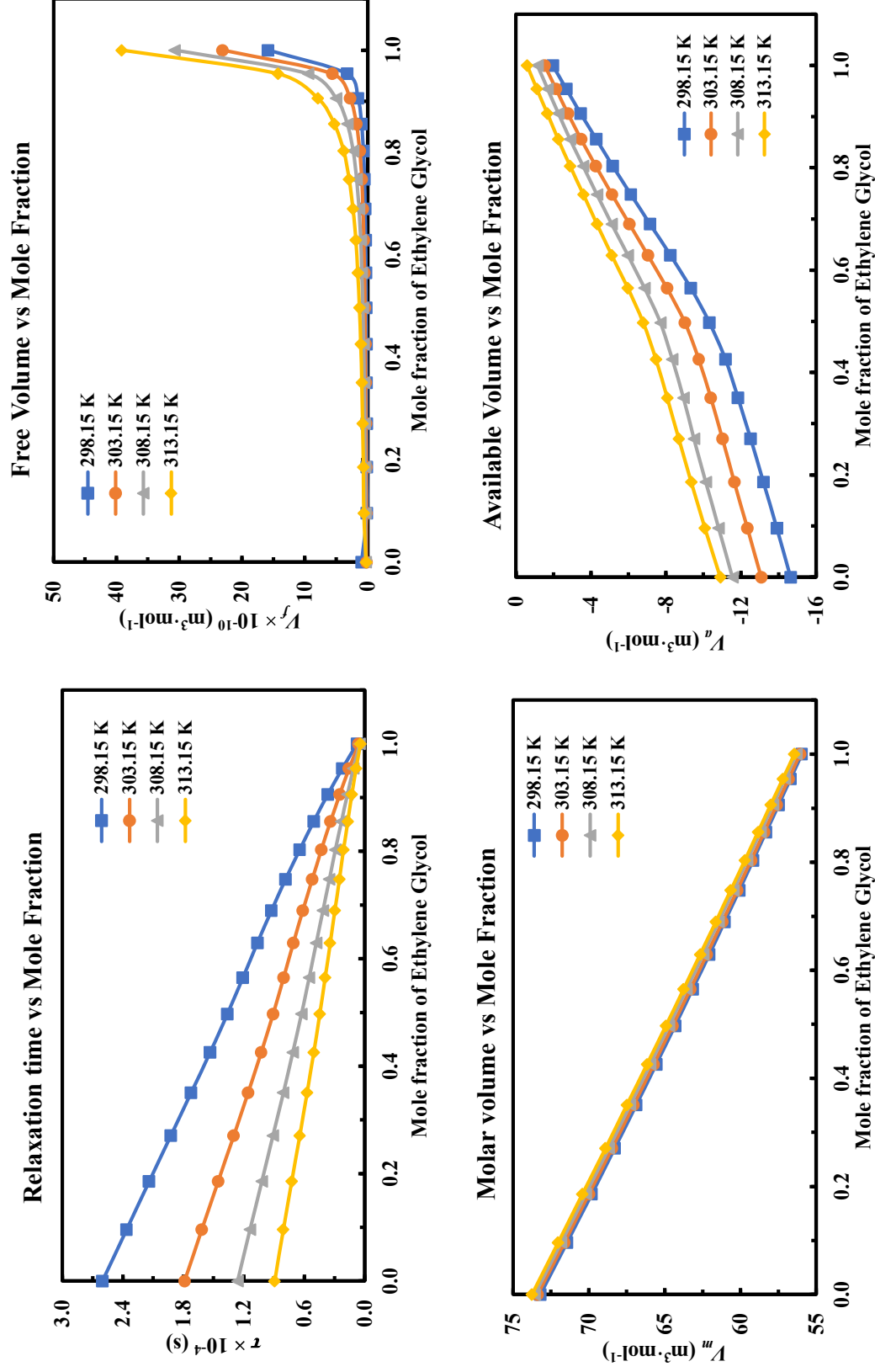


Figure 4.33: Plots of relaxation time, free volume, molar volume and available volume in the binary mixtures of Ethylene Glycol (1) + Glycerol (2).

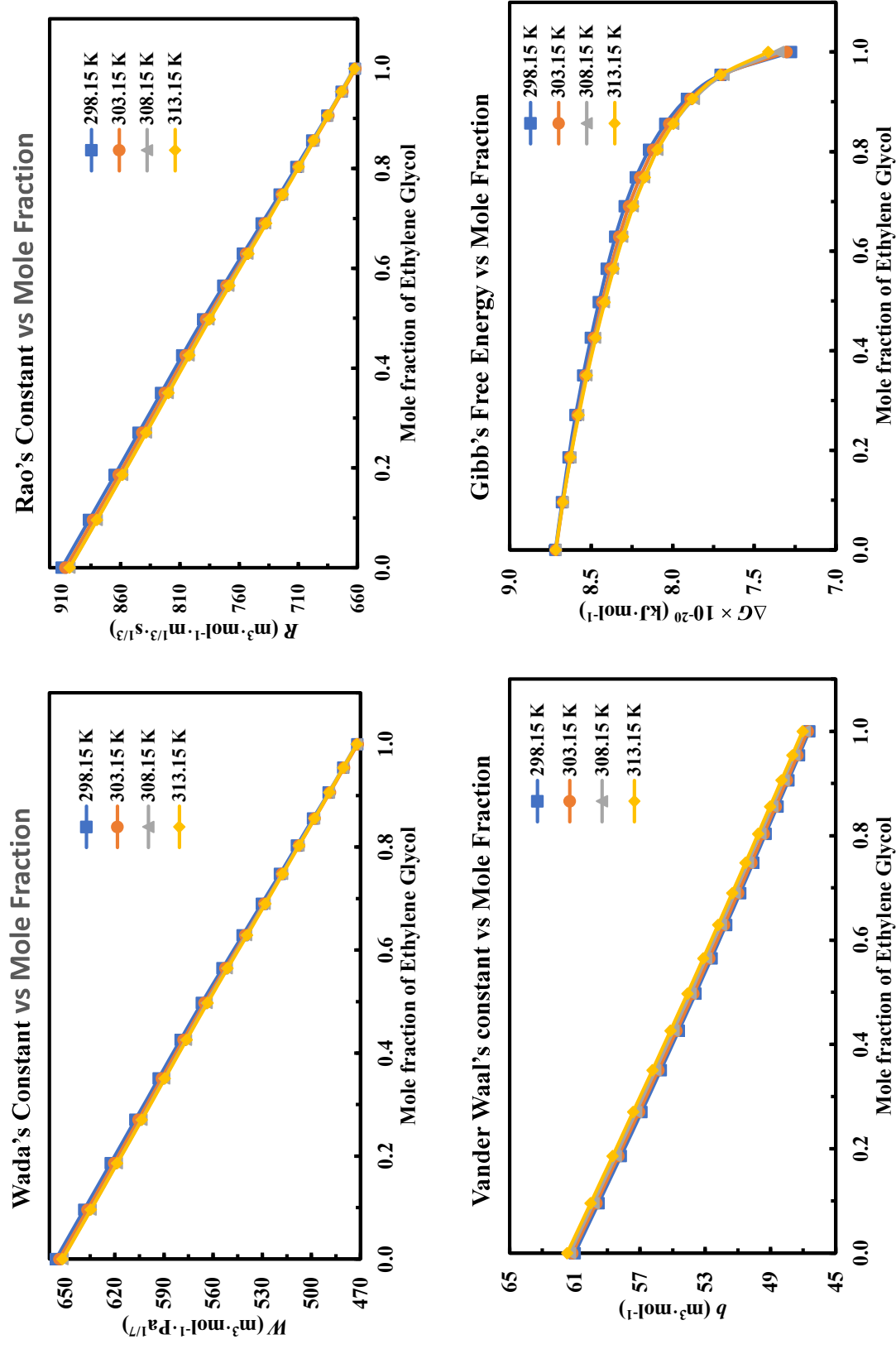


Figure 4.34: Plots of Wada's constant, Rao's constant, Vander Waal's constant and Gibbs's Free Energy in the binary mixtures of Ethylene Glycol (1) + Glycerol (2).

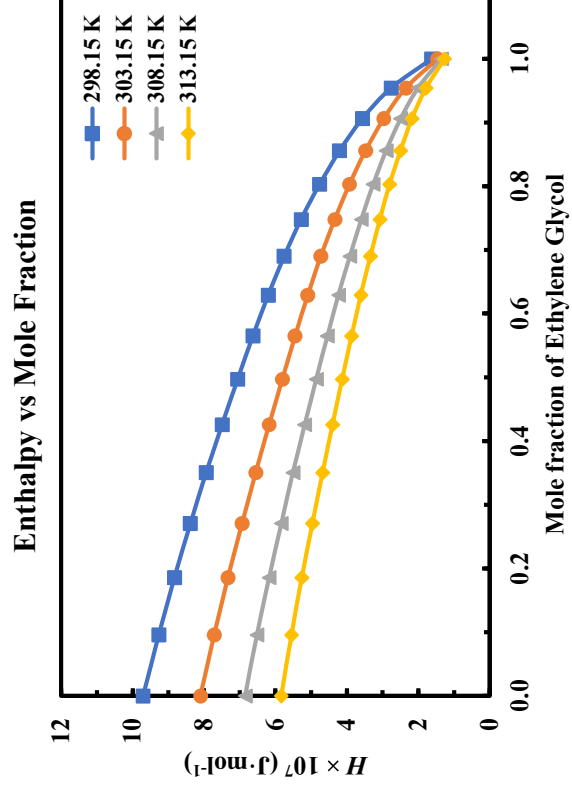
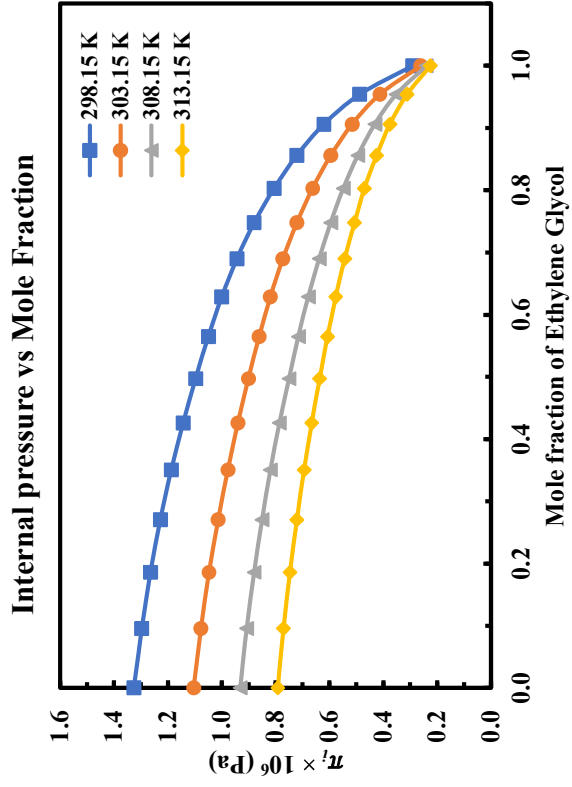


Figure 4.35: Plots of internal pressure and enthalpy in the binary mixtures of Ethylene Glycol (1) + Glycerol (2).

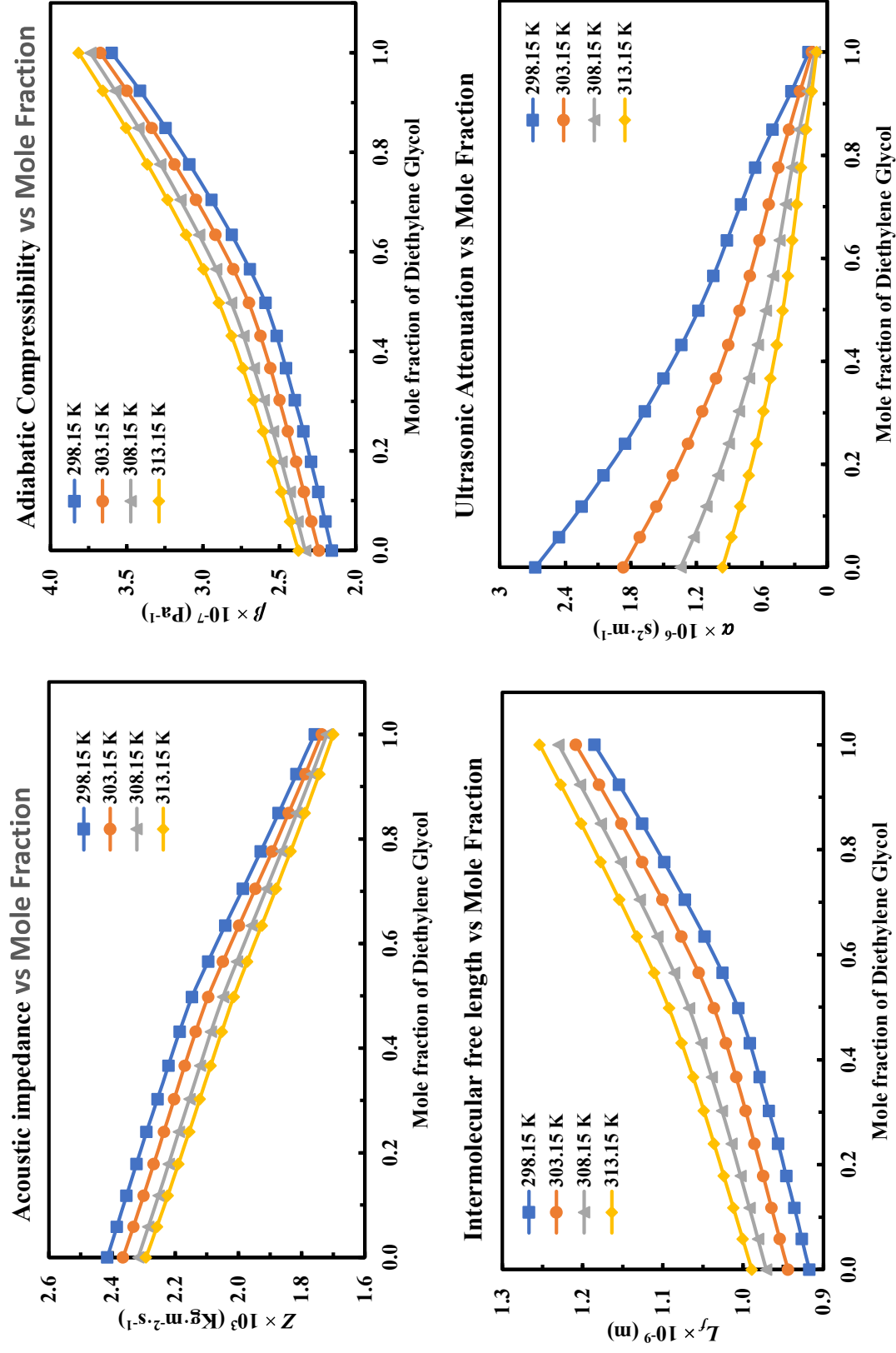


Figure 4.36: Plots of acoustic impedance, intermolecular free length and ultrasonic attenuation in the binary mixtures of Diethylene Glycol (1) + Glycerol (2).

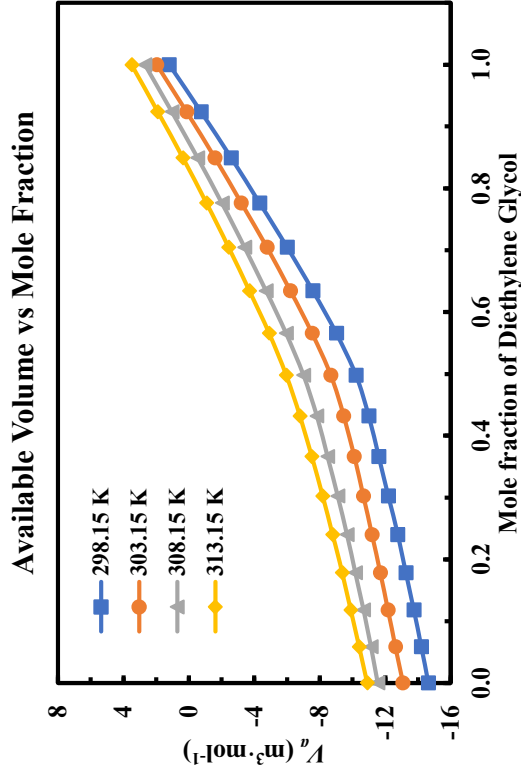
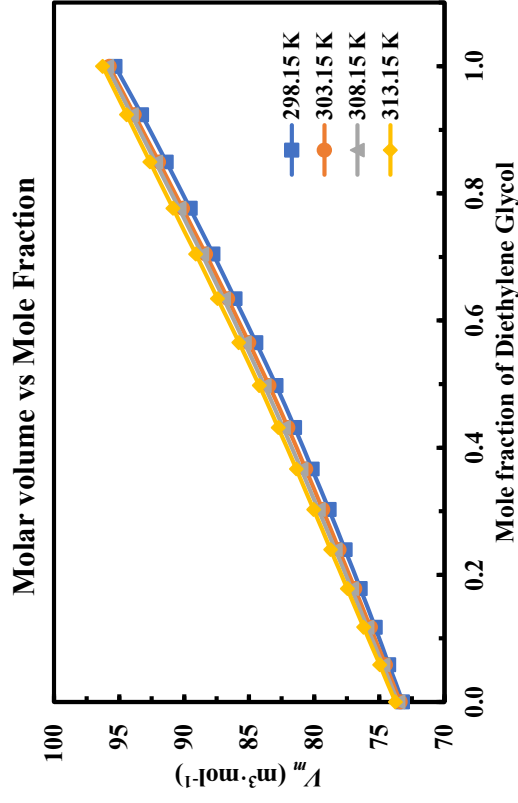
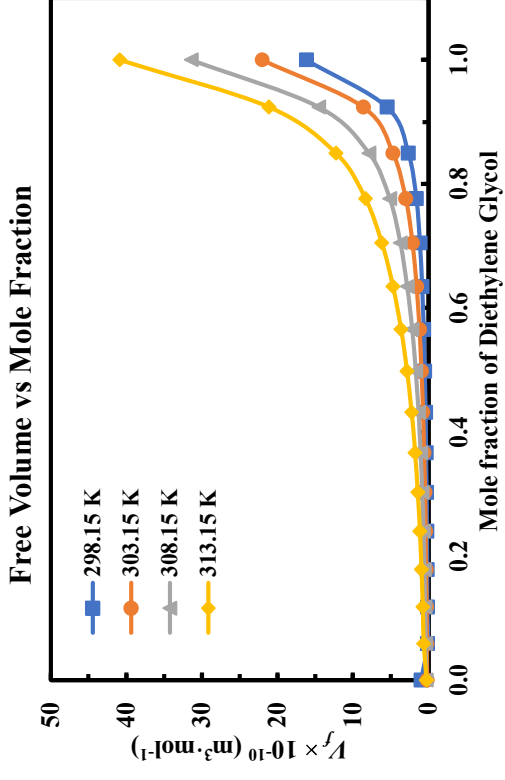
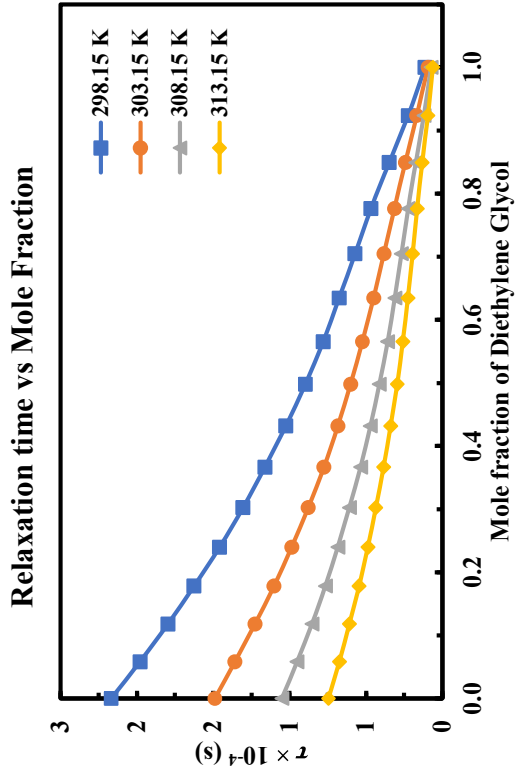


Figure 4.37: Plots of relaxation time, free volume, molar volume and available volume in the binary mixtures of Diethylene Glycol (1) + Glycerol (2).

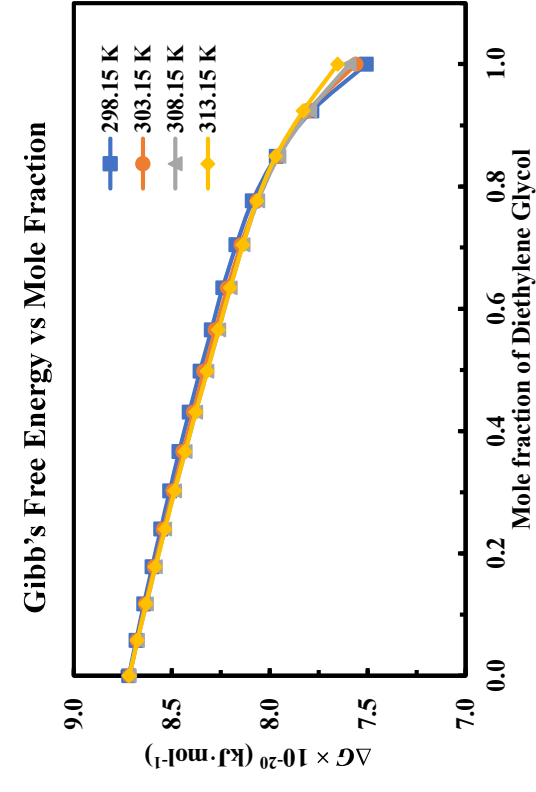
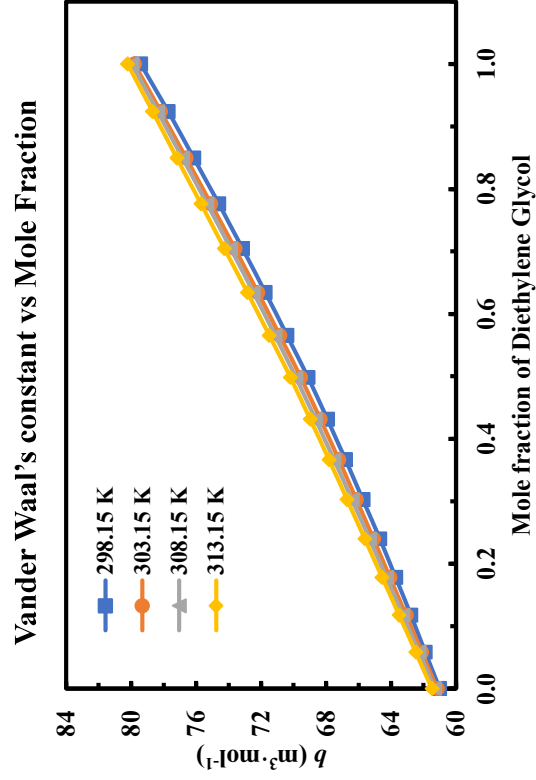
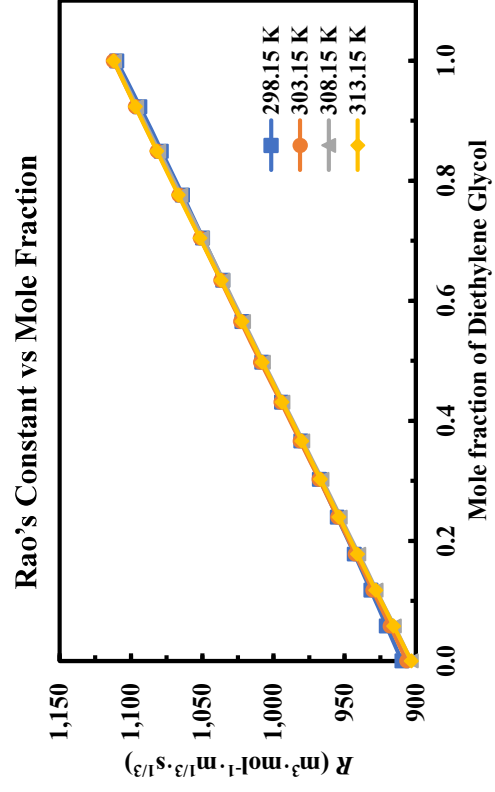
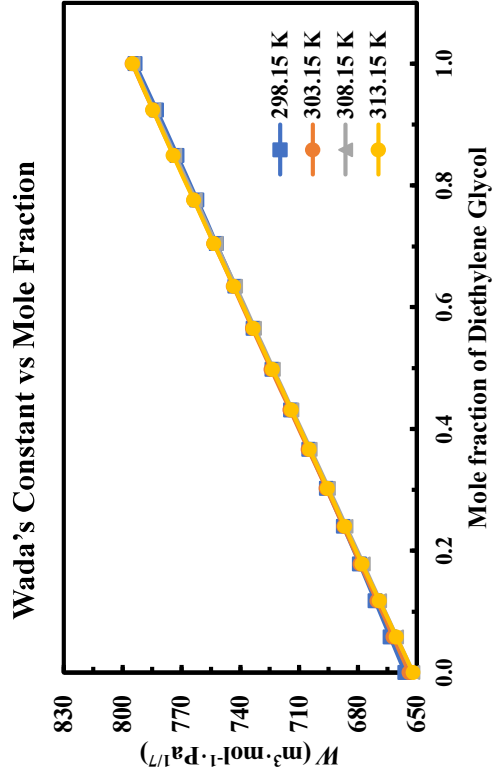


Figure 4.38: Plots of Wada's constant, Rao's constant, Vander Waal's constant and Gibb's Free Energy in the binary mixtures of Diethylene Glycol (1) + Glycerol (2).

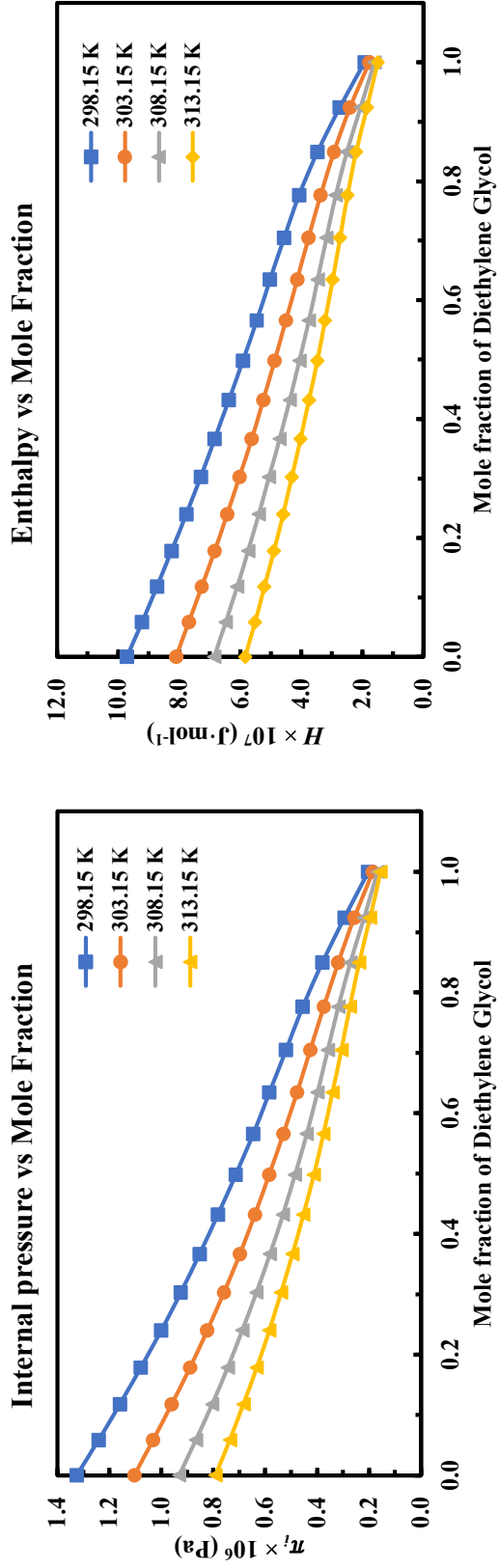


Figure 4.39: Plots of internal pressure and enthalpy in the binary mixtures of Diethylene Glycol (1) + Glycerol (2).

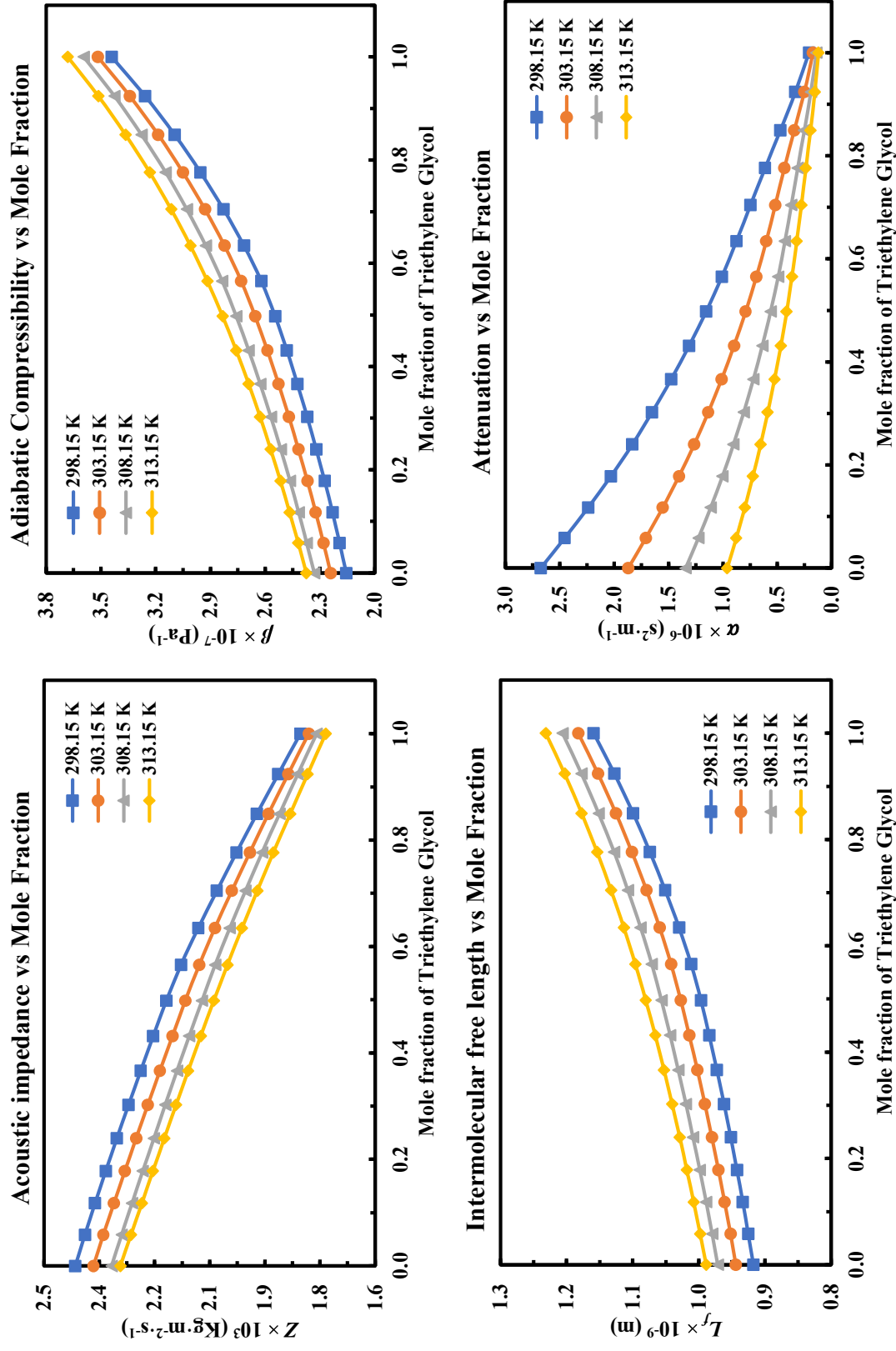


Figure 4.40: Plots of acoustic impedance, adiabatic compressibility, intermolecular free length and ultrasonic attenuation in the binary mixtures of Triethylene Glycol (1) + Glycerol (2).

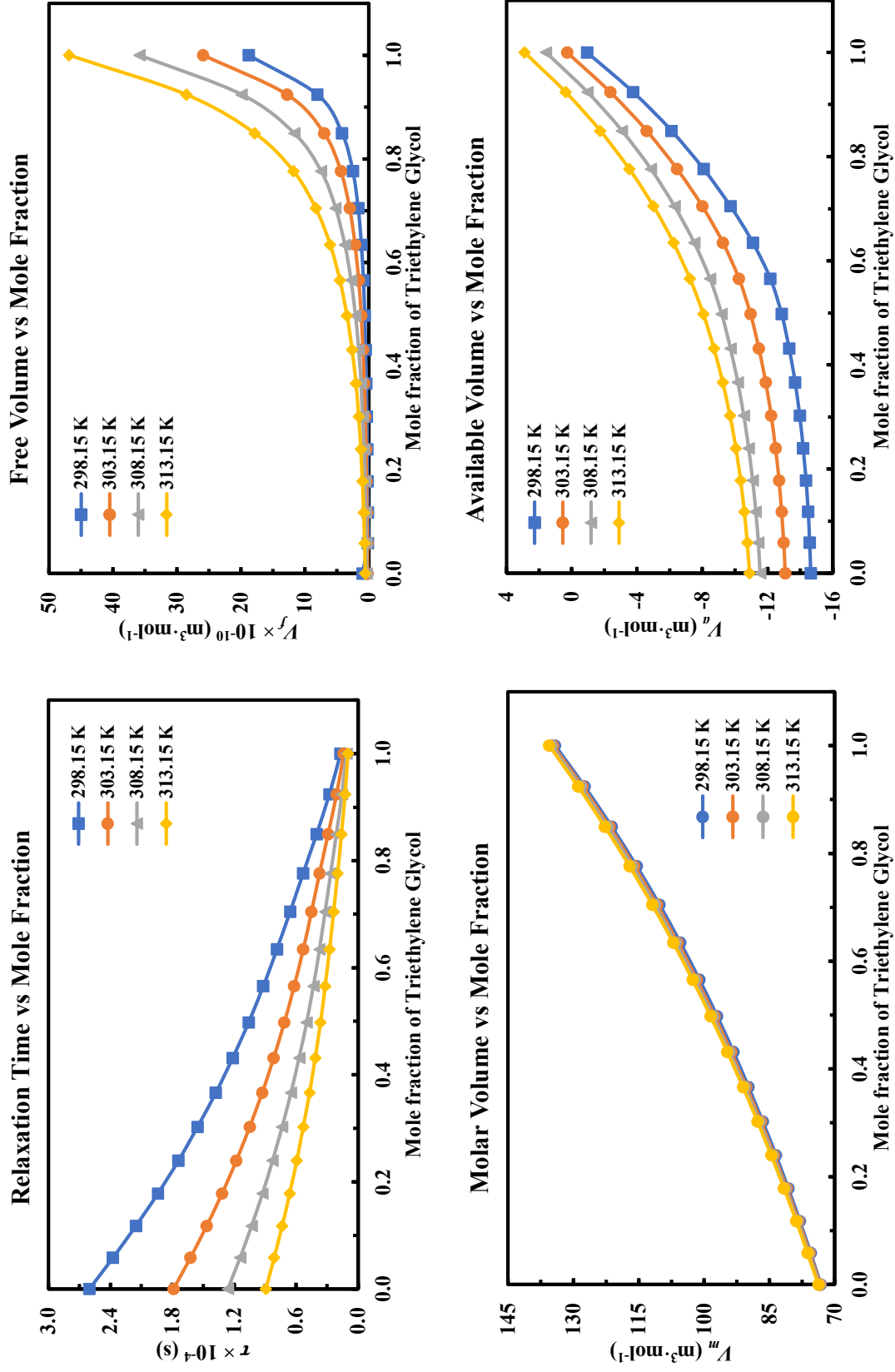


Figure 4.41: Plots of relaxation time, free volume, molar volume and available volume in the binary mixtures of Triethylene Glycol (1) + Glycerol (2).

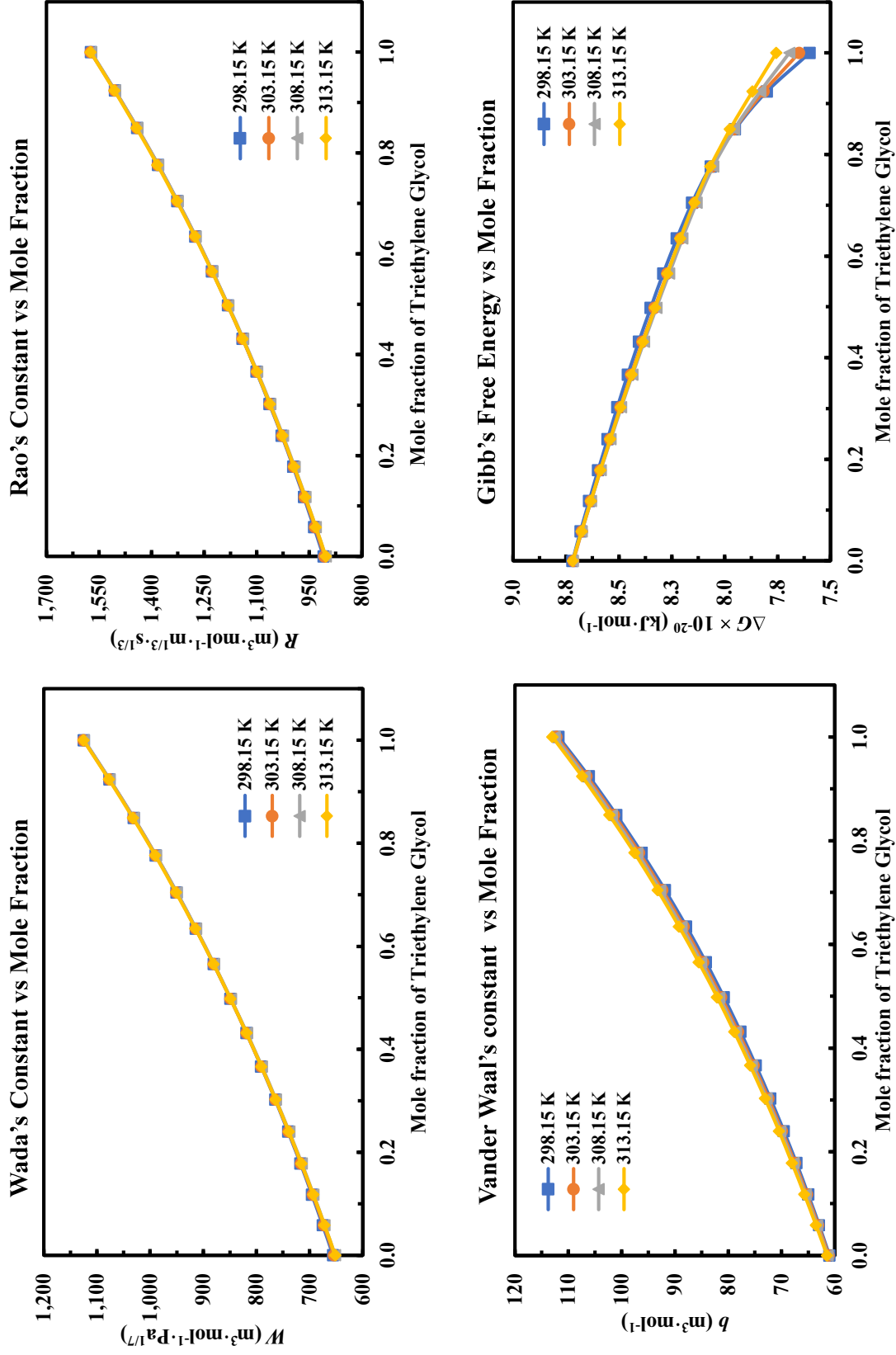


Figure 4.42: Plots of Wada's constant, Rao's constant, Vander Waal's constant, and Gibb's Free Energy in the binary mixtures of Triethylene Glycol (1) + Glycerol (2).

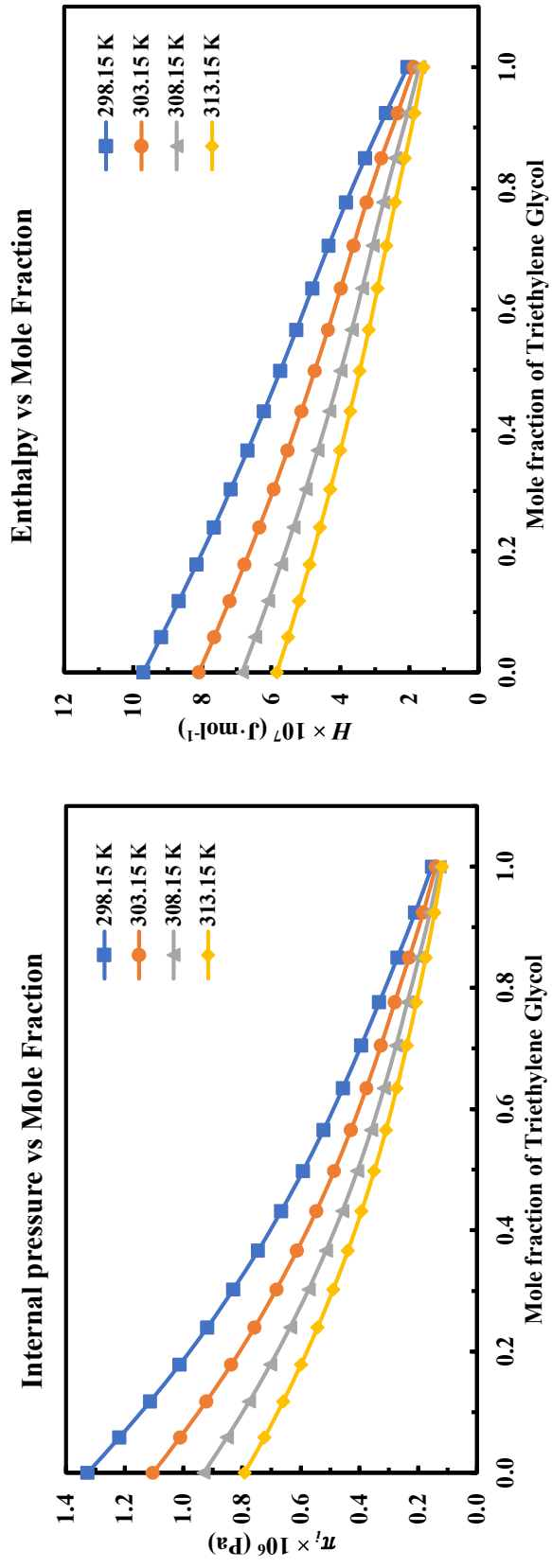


Figure 4.43: Plots of internal pressure and enthalpy in the binary mixtures of Triethylene Glycol (1) + Glycerol (2).

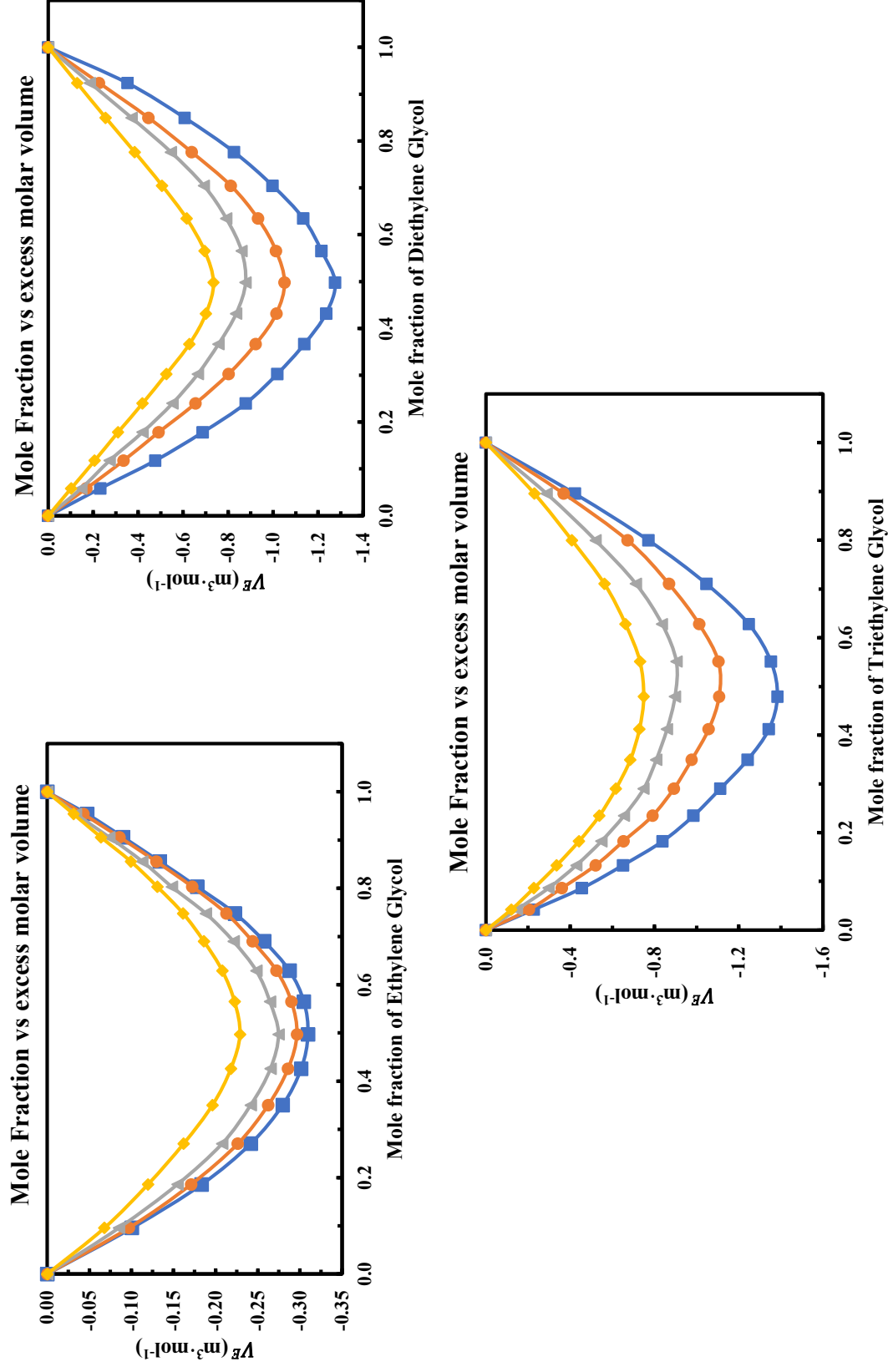


Figure 4.44: Plots of excess molar volume in binary mixtures of Ethylene Glycols (1) + Glycerol (2) at different temperatures [■, 298.15 K; ●, 303.15 K; ▲, 308.15 K; ◆, 313.15 K].

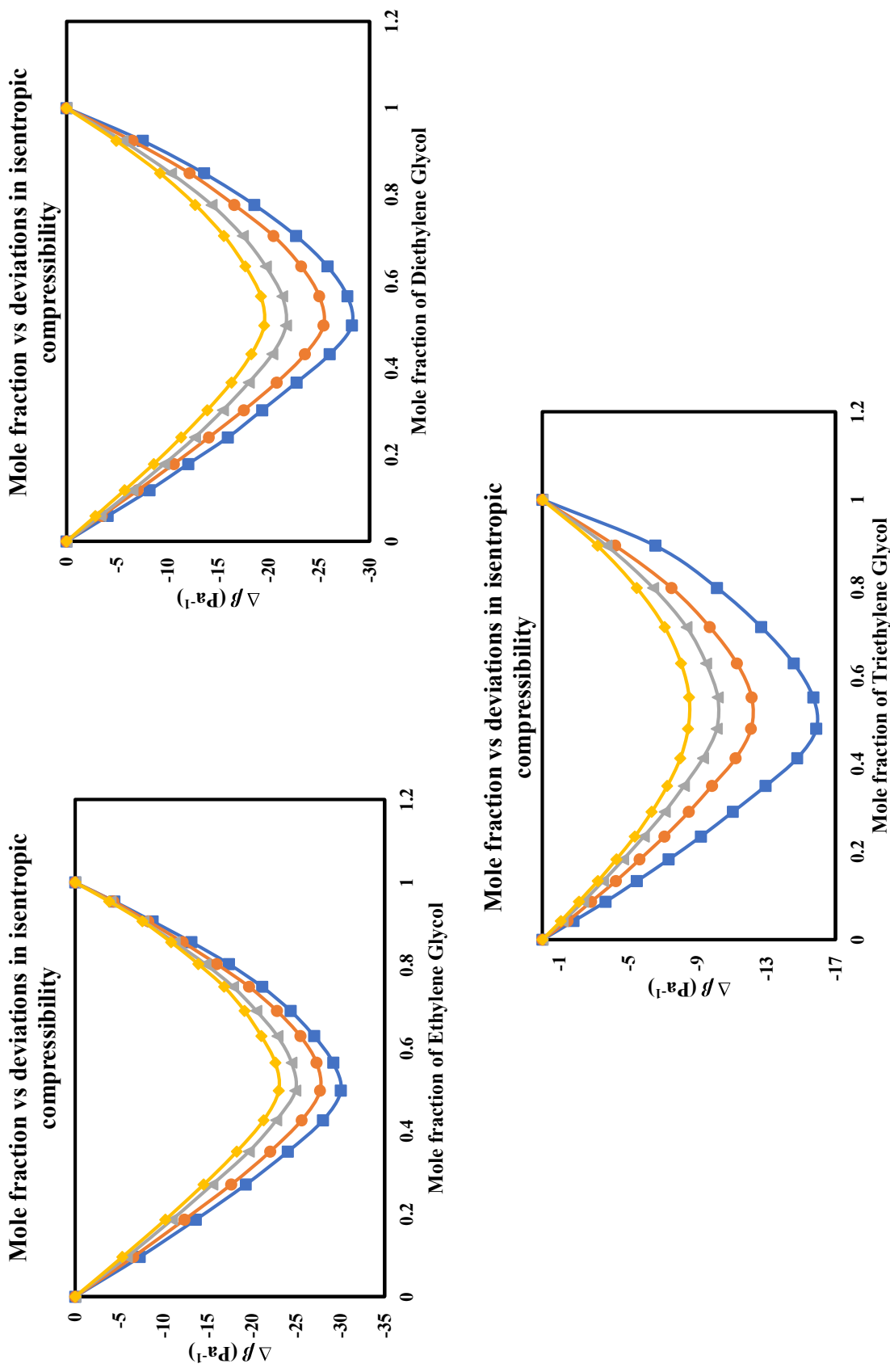


Figure 4.45: Plots of deviations in isentropic compressibility in binary mixtures of Ethylene Glycols (1) + Glycerol (2) at different temperatures [■, 298.15 K; ●, 303.15 K; ▲, 308.15 K; ◆, 313.15 K].

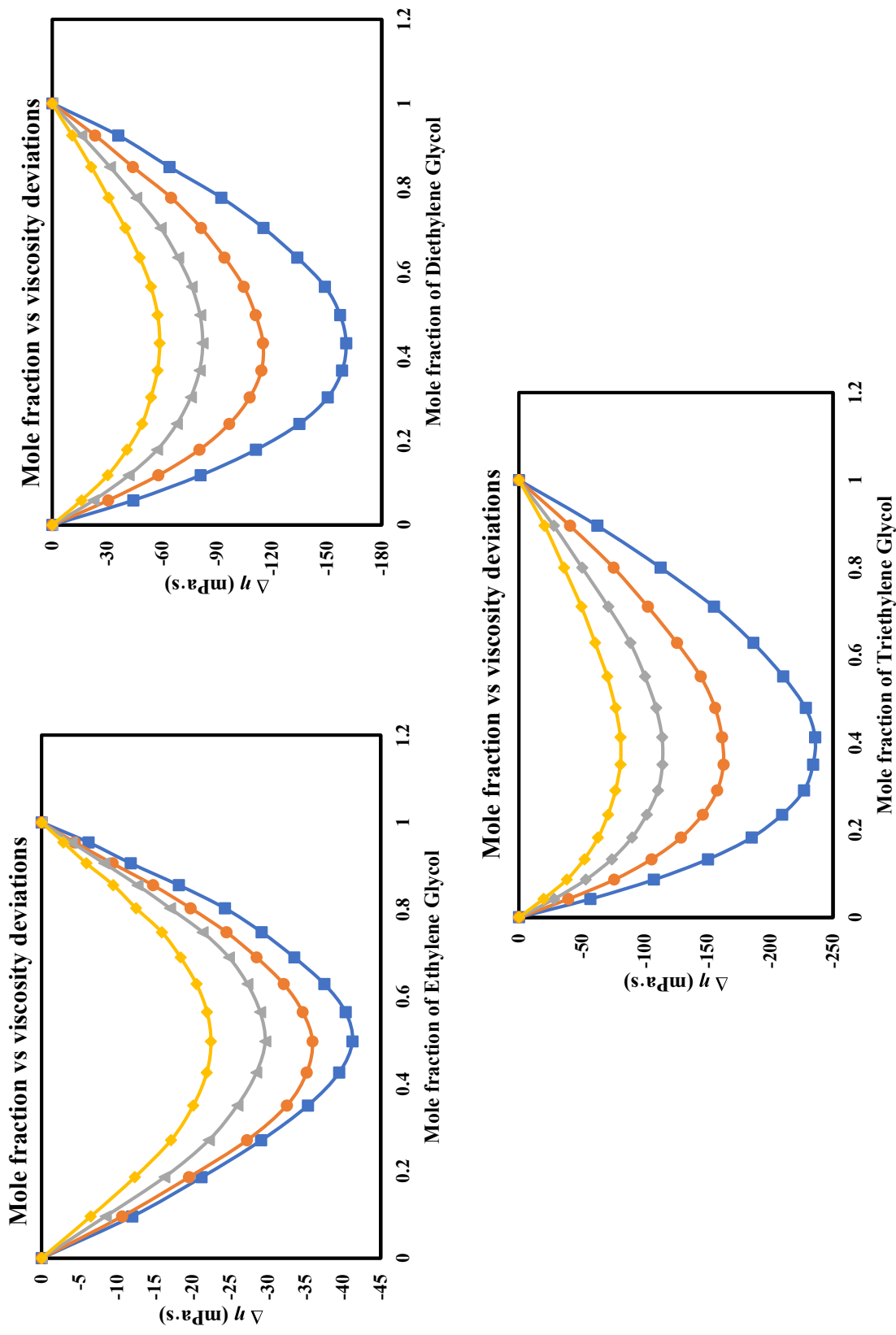


Figure 4.46: Plots viscosity deviations in binary mixtures of Ethylene Glycols (1) + Glycerol (2) at different temperatures [■, 298.15 K; ●, 303.15 K; ▲, 308.15 K; ◆, 313.15 K].

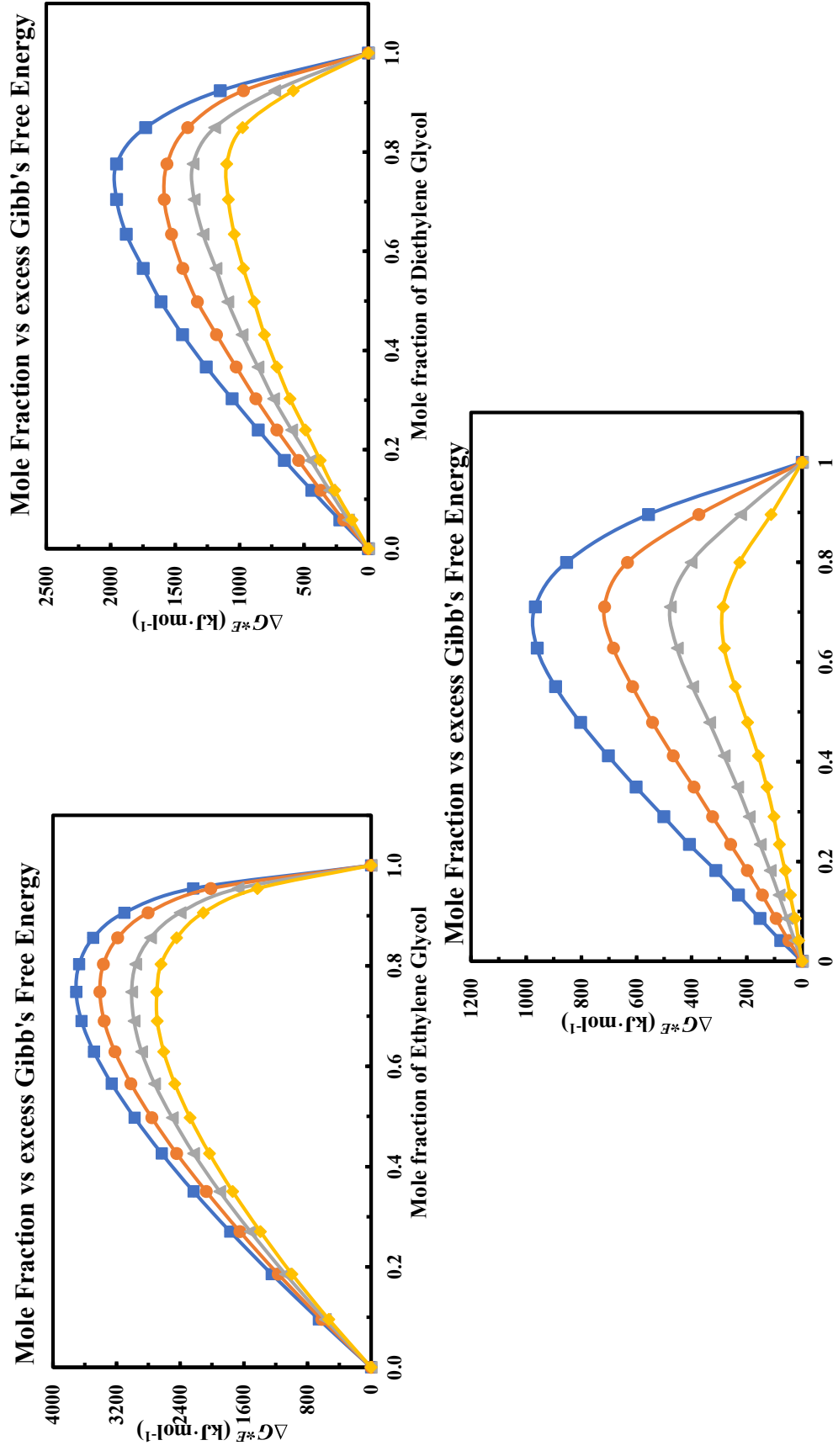


Figure 4.47: Plots of excess Gibbs's Free Energy in binary mixtures of Ethylene Glycols (1) + Glycerol (2) at different temperatures [■, 298.15 K; ●, 303.15 K; ▲, 308.15 K; ◆, 313.15 K].

Summary and Conclusion

The thesis entitled “ULTRASONIC, VOLUMETRIC AND VISCOMETRIC STUDY OF LIQUID MIXTURES CONTAINING GLYCOLS AT DIFFERENT TEMPERATURES” aims at describing the acoustical and thermodynamic behavior of the liquid mixtures comprising glycols. Glycols are the liquids which are miscible in water in the whole composition range. They are broadly used in plastic industry where they are used in the preparation of polyethylene terephthalate which is used further to make plastic bottles for pharmaceutical and food industry. In the present study we have made an attempt to study the intermolecular interactions among glycols and sugar alcohols by studying their thermodynamic properties. Sugar alcohols are a kind of ‘low digestible carbohydrate’, a group that comprises of fiber and resistant starch. These are used as a substitute to sugar in various diet foods (including soft drinks and ice cream), cough syrups, mints and sugar-free chewing gum and to store these diet foods various containers are used from plastic industry. Hence, thermodynamic study of glycols and sugar alcohols is of considerable importance. To study the thermodynamic properties of liquid mixtures the density, ultrasonic speed and viscosity of the mixtures have been measured at different temperatures with the help of different instruments namely Anton Paar DSA 5000 M, Specific gravity bottle, Mittal enterprises ultrasonic interferometer and Ostwald’s viscometer. Utilizing these measured parameters, apparent molar properties (apparent molar volume and apparent molar isentropic compression), partial molar properties (partial molar volume, partial molar isentropic compression and partial molar expansibilities), partial molar properties of transfer (partial molar volume of transfer and partial molar isentropic compression of transfer), the pair and triplet interaction coefficients are evaluated.

Various derived parameters such as acoustic impedance, adiabatic compressibility, intermolecular free length, relaxation time, ultrasonic attenuation, free volume, available volume, molar volume, Wada’s constant, Rao’s constant, Vander Waal’s constant, internal pressure, enthalpy and Gibb’s free energy are computed for binary mixtures of ethylene glycol + glycerol, diethylene glycol + glycerol and triethylene glycol + glycerol. To see the deviation of experimental ultrasonic speed from theoretical ultrasonic speed several theoretical models namely the theoretical ultrasonic speed model given by Nomoto, Van Dael and Vangeel, Junjie and the impedance-based

relation are incorporated. The excess thermodynamic properties have also been calculated for these binary systems which suggested the presence of strong molecular interactions in the binary mixtures.

Densities and speeds of sound of ethylene glycol, diethylene glycol, triethylene glycol in aqueous and aqueous solutions of glycerol have been reported at different temperatures, $T = (293.15, 298.15, 303.15 \text{ and } 308.15) \text{ K}$. Values of apparent molar volume, partial molar volume and partial molar volume of transfer are calculated and found positive at all concentrations and temperatures. Similarly, apparent molar isentropic compression and partial molar isentropic compression are computed and the values are found to be negative. All the calculated values of apparent molar and partial molar properties are increasing with rise in concentration of glycols as well as glycerol suggesting strong interactions among molecules of glycol and glycerol. The pair and triplet interaction coefficients suggest the pair-wise interactions among the glycerol and glycol molecules as the values of pair interaction coefficients are greater than triplet interaction coefficients. All the calculated values of ethylene glycols in glycerol follow the order: Ethylene glycol > Diethylene Glycol > Triethylene Glycol. Apparent molar volume and partial molar volume for Polyethylene Glycol-400 (PEG-400) and Polyethylene Glycol-4000 (PEG-4000) in $(0.00, 0.01, 0.03, 0.05, 0.07) \text{ mol}\cdot\text{kg}^{-1}$ aqueous solutions of glycerol at temperatures $T = (293.15, 298.15, 303.15, 308.15) \text{ K}$ have been found positive and rising with regard to upsurge in molality of PEGs and temperature which infers pronounced solute-solvent interactions. This surge is also perceived in relation with molar mass of PEGs that is with escalating molar mass of PEGs the apparent molar volumes also escalate at entire temperature range and for entire glycerol's concentrations ensuing extremum solute-solvent interaction in PEG-4000. The apparent molar isentropic compression and partial molar isentropic compression are found to be negative and these values become less negative with rise in temperature and concentration of glycerol which suggests robust solute-solvent interactions among molecules of PEGs and glycerol. The positive values of transfer properties indicate the structure making ability of solute in the solvent molecules. The interaction parameters for PEGs-glycerol solutions are calculated and values thus obtained showed that predominating interactions existed were mainly pairwise.

The apparent molar and partial molar properties for ethylene glycol, diethylene glycol and triethylene glycol in (0.00, 0.01, 0.03, 0.05) mol·kg⁻¹ aqueous solutions of sorbitol have been determined at temperatures $T = (288.15, 298.15, 308.15, 318.15)$ K. Values of apparent molar volume, partial molar volume, (partial molar volume and partial molar isentropic compression) of transfer are attained to be positive whereas apparent molar isentropic compression and partial molar isentropic compression for all three glycols are negative. All these obtained values are increasing with increase in temperature and concentration of glycols as well as sorbitol which infer strong interactions among EGs and sorbitol molecules. The partial molar expansibility values suggest the structure making ability of glycols in sorbitol solutions. The densities and speeds of sounds for PEG-400 and PEG-4000 in (0.00, 0.01, 0.03, 0.05) mol·kg⁻¹ aqueous solutions of sorbitol are measured at temperatures $T = (288.15, 298.15, 308.15, 318.15)$ K. Apparent molar volume, apparent molar isentropic compression, partial molar volume and partial molar isentropic compression, partial molar volume of transfer, partial molar isentropic compression of transfer and other parameters such as pair and triplet interaction coefficients, partial molar expansibilities and their second order derivatives have been determined. The positive and surging values of apparent molar volume and partial molar volume with rising concentration of sorbitol specify the existence of sturdy solute-solvent interactions amongst sorbitol and PEGs molecules. The apparent molar isentropic compressions and partial molar isentropic compressions are found to be negative which support the volumetric results.

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LIST OF PUBLICATIONS AND CONFERENCES ATTENDED

1. Nabaparna Chakraborty, Harsh Manchanda, **Kirandeep Kaur**, Kailash Juglan “Acoustic and thermodynamic study of D-Panthenol in aqueous solutions of glycol at different temperatures”, *Journal of Chemical Thermodynamics*. (2018), doi: 10.1016/j.jct.2018.07.006.
2. **Kirandeep Kaur**, Isha Behal, Kailash Juglan and Harsh Kumar; “Ultrasonic and volumetric studies on interactions of ethylene glycol, diethylene glycol and triethylene glycol in aqueous solutions of glycerol at temperatures $T = (293.15\text{K} - 308.15)\text{K}$ ”, *Journal of chemical thermodynamics*. 125 (2018) 93–106.
3. **Kirandeep Kaur**, Kailash Chandra Juglan and Harsh Manchanda; “Investigation on temperature dependent volumetric and acoustical properties of homologous series of glycols in aqueous sorbitol solutions”, *J. Chem. Eng. Data* (2017) 62, 3769-3782.
4. **Kirandeep Kaur** and K.C. Juglan; “Thermo-acoustical molecular interaction study in binary mixtures of glycerol and ethylene glycol at 293K”, *AIP Conference Proceedings* 1860, 020026 (2017); doi: 10.1063/1.4990325.
5. Priti Manon, K.C. Juglan, **Kirandeep Kaur**, Nidhi Sethi and J. P. Kaur; “Intermolecular interaction studies of glyphosate with water”, *AIP Conference Proceedings* 1860, 020018 (2017); doi: 10.1063/1.4990317.
6. **Kirandeep Kaur** and K. C. Juglan, “Experimental and theoretical study of ultrasonic velocity in binary liquid mixture of chloroform and methanol”, *Der Pharma Chemica*, 2016, 8(6):87-90.
7. **Kirandeep Kaur** and K. C. Juglan, “Ultrasonic velocity, density and viscosity studies of the binary mixtures of ethyl acetate with hexane”, *Journal of Chemical and Pharmaceutical Research*, 2016, 8(7):49-53.
8. **Kirandeep Kaur** and Kailash C. Juglan, “Studies of molecular interaction in the binary mixture of chloroform and methanol by using ultrasonic technique”, *Der Pharma Chemica*, 2015, 7(2):160-167.

Workshop / Seminars / Conferences / Certifications

- “Recent Advances in Experimental and Theoretical Physics”, Central University of Jammu, 17-18 April, 2018.
- “46th National Symposium on Acoustics”, Aligarh Muslim University, 28-30 October, 2017.
- “National seminar on Advances in Physical Chemistry” at PEC Chandigarh in March, 2017.
- “Recent Advances in Fundamental and Applied Sciences (RAFAS)” at LPU in 25-26 November, 2016.
- Workshop on recent researches in Chemical Sciences, NIT Jalandhar, 7-15 December, 2015.
- “Exploring Basic and Applied Sciences (EBAS)” at LPU in 14-15 November, 2014.
- “Bhartiya Vigyan Sammelan and Expo (BVS)” at LPU in 12-14 October, 2012.

Papers presented in conferences

1. **Kirandeep Kaur**, K.C. Juglan, Harsh Kumar, Isha Behal; “Experimental and theoretical study of molecular interactions in the binary mixtures of some ethylene glycols with glycerol”, *Recent Advances in Experimental and Theoretical Physics*, Central University of Jammu, 2018.
2. **Kirandeep Kaur**, K.C. Juglan, Harsh Kumar; “Thermo-acoustical molecular interaction study in binary mixtures of glycerol and ethylene glycol at temperature 298 K”, *46th National Symposium on Acoustics*, Aligarh Muslim University, 2017.
3. **Kirandeep Kaur**, K.C. Juglan, Harsh Kumar and Isha Behal; “Molecular interaction study in binary mixtures of glycerol and ethylene glycol at 295K”, *Advances in Physical Chemistry*, Punjab Engineering College, 2017.
4. **Kirandeep Kaur** and K.C. Juglan; “Thermo-acoustical molecular interaction study in binary mixtures of glycerol and ethylene glycol at 293K”, *Recent Advances in Fundamental*

and Applied Sciences, Lovely Professional University, 2016.

5. **Kirandeep Kaur** and K.C. Juglan; “Intermolecular interactions in the mixtures of chloroform and methanol at temperature 298K”, *Exploring Basic and Applied Sciences*, Lovely Professional University, 2014.

Papers communicated

1. **Kirandeep Kaur**, K. C. Juglan, Harsh Kumar “Temperature dependent physicochemical studies of polyethylene glycols (PEG-400 and PEG-4000) in aqueous sorbitol solutions”, *Journal of Molecular Liquids*.
2. **Kirandeep Kaur**, Kailash Juglan, Harsh Manchanda “Acoustical and volumetric investigation of polyethylene glycol 400 and polyethylene glycol 4000 in aqueous solutions of glycerol at different temperatures”, *Journal of Chemical Thermodynamics*.
3. **Kirandeep Kaur**, Kailash Juglan and Harsh Kumar “Thermodynamic interactions study of some ethylene glycols with aniline in aqueous medium at different temperatures: An acoustical and volumetric approach”, *Journal of Chemical and Engineering Data*.
4. Ashima Thakur, Kailash Juglan, Harsh Manchanda, **Kirandeep Kaur** “Apparent molar properties of glycols in methanol solutions of propyl 4-hydroxybenzoate (propylparaben) at T= (293.15 to 308.15) K: An acoustic and volumetric approach”, *Journal of Molecular Liquids*.